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International Journal for Research in Applied Science & Engineering Technology (IJRASET) Fractionation of Heavy metals In Sediments of Cauvery River, Karnataka, India

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Abstract: Majority of heavy metals resulting from anthropogenic sources in Southern India reaches the River Cauvery, which acts as one of the sinks in the region. This study attempts to document the heavy metal concentrations in the sediments of Cauvery river, Karnataka, India, with emphasis on chemical fractionation. The pollution of sediments by heavy metals has assumed as a serious concern due to their toxicity and accumulative behavior. Changes in environmental conditions can strongly influence the behavior of both essential and toxic elements by altering the forms in which they occur and therefore quantification of the different forms of metal is more meaningful than total metal concentrations. In this study, fractionation of metal ions in sediments of the Cauvery River, Karnataka, India, has been studied to determine the Eco toxic potential of metal ions.

Key Words: River Sediments, heavy metals, metal fractionation, sequential extraction, Cauvery River

I. INTRODUCTION

River sediments are basic components of our environment as they provide nutrients for living organisms and serve as sinks for chemical species (Gomez-Ariza *et al.*, 1999). Freshwater ecosystems in India are largely exploited for domestic and industrial activities and also for disposal of wastes. In particular, contamination caused by heavy metals is a major concern today due to their long lasting potential and toxicity. The adverse ecological effects of contaminants in sediment include skin lesions, increased tumor frequency and toxicity in fish, reproductive failure in fish eating birds and mammals and decreased biodiversity in aquatic ecosystem. Threats to human health occur when sediment contaminants bioaccumulate in fish and shellfish tissues consumed by humans (Mulligan *et al.*, 2001). Although predominant sources of these metals in sediments are weathering, volcanic eruptions, anthropogenic activities such as agricultural practices, metallurgical process, industrial activities, mining operations, fuel emissions, discharge of domestic sewage and solid waste disposal contribute to elevated levels of heavy metals. Heavy metals are usually present in different chemical forms which determine their mobility and bioavailability (Lopez-Sanchez *et al.*, 1993; Weisz *et al.*, 2000; Kuang-Chung *et al.*, 2001). The fractionation is influenced by the physico-chemical conditions in the local environment such as pH, redox conditions and absorption sites among metal ions and absorptive area. In general, the mobility and bioavailability of metals decrease in the order of exchangeable > carbonate bound > Fe-Mn oxide bound > organic matter bound > lithogenic fraction (Prusty *et al.*, 1994).

The study of metal speciation in the environment is important in developing countries like India since traffic, industrial activity and mining operations to accelerate the discharge of heavy metals. Dry and wet deposition of metals in local and regional water resources are also in the increased rate. A majority of heavy metals released from anthropogenic sources reaches the river which acts as sinks. It is extremely essential to determine the anthropogenic derived metals fractionate in the sediments. Speciation studies in sediments act as a useful indicator of long and medium term metal flux in industrialized estuaries and rivers and they help to improve management strategies as well as to assess the success of recent pollution control programs (Ravichandran *et al.*, 1995). Although heavy metals are very rare. It will be further interesting to know the chemical fractionation of heavy metals in the Cauvery river sediments. In that context, present work attempted to determine the distribution and geochemical fractionation of six heavy metals (Cr, Ni, Fe, Cu, Zn and Pb).

Sediment characteristics play a significant role in the chemical forms of the metals present in the sediments. A significant association with the residual fraction (F5 and F6) and a scavenging action by the Fe-Mn oxide fraction of the sediments were observed in Jhanji River (Baruah *et al.*, 1996). Sediment particle size also influenced the distribution of heavy metal in various

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fractions (Tsai et al., 2003).

II. SPECIATION OF HEAVY METALS IN SEDIMENTS

Speciation analysis is the analytical technique of identifying and/or measuring the quantities of one or more individual chemical species in a sample. The chemical species are specific forms of an element defined as to isotopic composition, electronic or oxidation state, and/or complex or molecular structure. The speciation of an element is the distribution of an element in defined chemical species in a system. In case that it is not possible to determine the concentration of the different individual chemical species. Fractionation is the process of classification of an element or a group of from a certain sample according to physical or chemical properties.

Speciation of heavy metal is greatly influenced by the chemical composition of sediments. Other factors which influence speciation are pH, hardness, and organic matter. Some metals such as Cadmium can be released from their organic complexes by increasing Cl (Chlorine) concentrations, which form chloride complexes. Experiments with Copper their toxicity and bioavailability correlates with the concentration of free metal concentration. Sediments are the complex chemical environment than water and there is no reliable method for assessing bioavailability of metals. It has been observed that the heavy metals in soil environment associated with several distinct geochemical phases such as clay minerals, organic matter, carbonates and sulphates.

Speciation of heavy metals can be observed at low pH induces dissolution, ion exchange and desorption reactions. Rajendran *et al.* (1992) in their study, the physico-chemical factors controlling the iron and manganese speciation in Skagerrak sediments (northeastern North Sea) observed that Mn in carbonate phase is negatively correlated to CaCO₃.

III. MATERIALS AND METHODS

A. Study Area

Cauvery River is one of the major river in India. The river leaves the Kodagu hills and flows on the Southern part of India. River Cauvery starts at Talacauvery in Madikeri district of Karnataka; it passes through the south interior Karnataka and is joined by many other smaller rivers. Mysore and Mandya districts of Karnataka being completely fed by this river-pass through Sangama/Mekedatu as the last point in Karnataka and enter Tamilnadu at Hogenakkal falls. The river passes through the dam at Mettur and joins Bhavani near Erode and again through the southern Tamilnadu areas of Trichy after which it branches itself into many other rivers. River Cauvery joins the Bay of Bengal at Poompuhar in Nagapattinam district. Kollidam is one of the tributaries where the excess flood water is released into in Tamilnadu (Fig.1)

Krishnarajasagara reservoir (KRS DAM) is the largest dam built on the river Cauvery in Karnataka. It is around 12km from Mysuru. KRS is located in Mandya district across river Cauvery near Kannambadivillage (latitude $12^0 25' 30''$ N, Longitude $76^0 34' 30''$ E) Cauvery river originates at Talakaveri in the Western Ghats in the state of Karnataka, flows generally south and east through Karnataka, and there is so many tributaries, drainage and branches. This research is carried out around the KRS dam and downstream of the river. There is huge irrigation, agricultural and industrial basin around the dam and river. This study was performed in nine stations (Fig.2) and showed in the Table No.1.

B. Sampling and pre-treatment of the sample

The sediment samples were collected (up to 5 cm depth) from Nine locations (Table 1) in the Cauvery River. Sediment samples were air dried at room temperature and homogenized using an agate mortar and pestle and sieved using a 63 micron mesh sieve. Then they were stored in polythene covers at room temperature. The sediment samples were analyzed for heavy metals speciation.

C. Multi-step sequential extraction

The sequential extraction procedure used in this study is Tessier *et al.* (1979) method. According to Tessier *et al.* heavy metals are associated with the fractions as described as follows:

1) The exchangeable fraction, which is likely to be affected by changes in water ionic composition as well as sorption-desorption processes;

2) The carbonate fraction, that is susceptible to changes in pH;

- 3) The reducible fraction, that consists of iron and manganese oxides which are unstable under anoxic conditions;
- 4) The organic fraction, that can be degraded leading to a release of soluble metals under oxidizing conditions and
- 5) The residual fraction that contains mainly primary and secondary minerals, which may hold metals within their structure.

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The extraction was carried out progressively on an initial mass of 1.00 g of sample of sediment samples. The samples for sequential extraction were dried in an oven at 60°C for 24 h in order to avoid, as far as possible, the transformation of some chemical forms (exchangeable and carbonate).

The selective extractions were conducted in 50 ml capacity centrifuge tubes. After each extraction step, the sample was subjected to 30 min of centrifugation at 4,000 rpm, the supernatant was separated from the residue with a pipette and transferred into a 25-ml calibrated flask. The residue was centrifugation and later washed thoroughly, the obtained second supernatant was added to the flask, which was diluted to the desired volume. The extracts obtained were acidified using aquaregia and stored in stopper polyethylene vessels until their analysis by using Atomic Absorption Spectroscopy (AAS). The total content of metals was determined after digesting 0.4 g of sample with aquaregia. The concentration of particular heavy metals was expressed per 1 kg of air dry sample.

D. Results and Discussion

Speciation of heavy metals was carried out according to Tessier method as described earlier. Table 2 shows the results of different fractions of the heavy metals in sediments of the Cauvery river. The exchangeable fraction (F1) contains metal elements in the ionic form, which have a high mobility and can be drained by water. The fraction related to the carbonates (F2) is extractable and can be accumulated in the plants. The fraction related to the oxides of iron and manganese (F3) and that related to organic matter (F4) contain metals enclosed in the matrix. The fraction (F5) contains the inert metals (Fig.3 to Fig.11).

The result shows that, the Iron occurred mainly in the residual fraction which is varied between 74.26% at station no.8 and 74.29% at station no.7 and in the organic matter fraction the concentration was observed between 17.31% to 17.34%. Iron was bound in smaller amounts in the form of oxides fraction which is ranged from 7.70% to 7.71%. The only minor concentration of iron was detected in the exchangeable and bound to carbonate fractions.

The speciation study shows that, the exchangeable fraction the Zinc metal was below the detection limit (BDL). In the fraction of hydrated oxides of iron and manganese the concentration ranged between 42.56% to 53.88% and it was bound to organic matter fraction in the concentration of 23.32%–24.34%. The amount of zinc in the residual fractions was varies between 17.23%- 23.07.

Nickel was found in the fraction bound to organic that has varied from 11.05%-12.02%, whereas 69.94 % to 85.63 in residual fraction. Bounded to oxide metal fraction for Nickel is 17.96% - 18.28% and BDL in carbonate bound fraction. The level of Nickel found in exchangeable metal fraction is once again lower than the detection limit

The analysis of sediment sample shows that, Copper in the different sediment samples have been found in organic matter fraction ranged from 78.57% to 79.59% and varied in the range of 20.40% - 21.42 % in residual form. The level of Copper in the exchangeable, carbonate fraction and fractions bound to hydrated oxides of iron and manganese was lower than the detection limit. Copper is bound much more tightly by residual fraction than Ni and is much less likely to be displaced by the hydroxylamine hydrochloride reagent. Similar results are reported by McLaren and Clucas (2001).

The speciation analysis shows that Chromium in the sediment sample is mainly found in the residual fraction with the range of 54.34% to 70% and slight lesser range of 26.08% - 31.91% bound to the organic matter. Whereas only smaller amounts of Chromium was present in hydrated iron and manganese oxides fractions with the range between 6.66% to 19.56%

The Lead concentration was observed in the range of 19.19% to 28.9% in the carbonate fraction, whereas in the oxides of iron and manganese oxide it was 26.01% to 40.96. For the organic matter fraction it was 17.50% to 25.90% and in the residual fraction with the range between 1.20% to 42.81%.

IV. CONCLUSION

Cauvery River is a major source for drinking water in the southern part of Karnataka state, India. Cauvery River is a good example for receiving the pollutants both from natural (lithogenic) and anthropogenic activities. The major sources of pollution of the Cauvery River are the agricultural runoff, municipal and domestic sewage and some of the industrial discharges. The heavy metals entering the ecosystem may lead to geoaccumulation, bioaccumulation, and biomagnifications that may have possibilities for environmental transformation into more toxic due to its mobile nature in its ionic form. The presences of heavy metals are the indicators for changes takes place in the water and the sediment environment. In this research work, the sediment character was determined and identified certain toxic heavy metals through the speciation study. The heavy metals mobility is little low in the exchangeable metal fraction and carbonate bound metal fractions. But in the Fe– Mn oxide metal fraction and organic and sulfide

metal fractions mobility of the metals are comparatively higher than the other fraction. The residual fraction has the high metal concentration in almost all the sediment samples. If the mobility of the metal is higher in initial two fractions of speciation study, that indicates its higher toxicity due to the mobility of the metal ions in the ecological food chain. In present study the heavy metals concentration is nearer to maximum levels in the sediments of Cauvery River. Once the concentration of heavy metals reaches the maximum level in the river basin, it would circulate among the aquatic organisms and it results in bioaccumulation in the nature. From the different processes of the industries, release of toxic chemicals, waste water, dumping of untreated solid waste to the surrounding environment leads to release of heavy metals. All these above said pollution problems are arising from the increased industrial activities/process and more usage of chemical fertilizers in the agricultural field.

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Table No.1: Sampling stations during the study period.

Station code	Sampling stations
D1	KRS dam
D2	Reservoir
R1	Dam gate
R2	Near dike of garden
R3	First bridge after dam
R4	Balmuri
R5	Birds sanctuary
R6	Srirangapatna bridge
R7	Sangama / Nimishamba temple

Table 2: Speciation of Heavy metals in sediment sample

(All fractions are expressed in mg/kg)

D1								
	Ι	II	III	IV	V			
Cu	BDL	BDL	BDL	3.9	1.0			
Cr	BDL	BDL	0.25	0.96	2.0			
Pb	BDL	6.8	9.6	6.1	11.6			
Zn	BDL	0.7	13.5	6.1	4.8			
Ni	BDL	ND	5.9	3.9	22.9			
Fe	10.1	13.1	260.5	585.4	2507.5			
D2								
Cu	BDL	BDL	BDL	3.2	0.8			
Cr	BDL	BDL	BDL	1.1	2.0			
Pb	1.4	6.5	9.1	5.8	11.0			
Zn	BDL	0.8	14.3	6.5	5.1			
Ni	BDL	BDL	6.7	4.4	26.1			
Fe	11.6	15.1	298.4	670.5	2872.1			
R1								
Cu	BDL	BDL	BDL	3.5	0.9			

Cr	BDL	BDL	0.23	0.9	1.9
Pb	BDL	8.0	11.2	7.2	13.6
Zn	BDL	0.9	16.3	7.4	5.8
Ni	BDL	BDL	7.3	4.8	28.5
Fe	12.3	16.0	317.4	713.2	3055.1
R2					I
Cu	BDL	BDL	BDL	6.1	1.6
Cr	BDL	BDL	0.95	1.2	2.5
Pb	0.8	5.8	8.1	5.2	9.8
Zn	BDL	1.1	19.8	8.9	7.1
Ni	BDL	BDL	8.1	5.4	31.6
Fe	11.0	14.4	284.3	638.8	2736.5
R3		•			•
Cu	BDL	BDL	BDL	6.4	1.7
Cr	BDL	BDL	BDL	1.5	3.2
Pb	BDL	6.1	8.5	5.4	10.3
Zn	BDL	0.7	12.4	5.6	4.4
Ni	BDL	ND	6.6	4.4	25.6
Fe	11.2	14.5	288.1	647.3	2772.8
R4		•			·
Cu	BDL	BDL	BDL	6.6	1.8
Cr	BDL	BDL	BDL	1.0	2.2
Pb	0.53	4.86	6.8	4.3	0.2
Zn	BDL	0.9	16.6	7.5	5.9
Ni	BDL	BDL	8.0	5.3	31.1
Fe	11.4	14.8	293.8	660.1	2827.6
R5		·			•
Cu	BDL	BDL	BDL	7.4	2.0
Cr	BDL	BDL	BDL	1.2	2.8
Pb	BDL	7.4	10.1	ND	13.1
Zn	BDL	1.2	21.7	9.4	8.0
Ni	BDL	BDL	6.1	3.7	23.6
Fe	13.5	17.6	348.2	782.4	3357.5
R6					•
Cu	BDL	BDL	BDL	6.9	1.8
Cr	BDL	BDL	BDL	1.1	2.4
Pb	BDL	7.0	9.4	6.6	12.4
Zn	BDL	1.9	20.8	9.2	6.8
Ni	BDL	BDL	6.6	4.0	25.5
Fe	10.2	13.3	262.9	590.7	2530.5
R7	-	1			1
Cu	BDL	BDL	BDL	7.7	2.1
Cr	BDL	BDL	BDL	1.2	2.7
Pb	0.9	7.6	10.3	7.2	13.6
Zn	BDL	2.0	22.2	9.9	7.1
Ni	BDL	BDL	7.2	4.4	28.2
Fe	11.8	15.4	305.2	685.7	2937.3

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Figure 1: Map of Cauvery River basin in India



Figure 2: Map of sample location sites around K.R.S. dam of cauvery River Basin



Figure 3. Speciation of heavy metals in sediment at D1 station



Figure 4. Speciation of heavy metals in sediment at D2 station



Figure 5. Speciation of heavy metals in sediment at R1 station



Figure 6. Speciation of heavy metals in sediment at R2 station



Figure 7. Speciation of heavy metals in sediment at R3 station



Figure 8. Speciation of heavy metals in sediment at R4 station



Figure 9. Speciation of heavy metals in sediment at R5 station



Figure 10. Speciation of heavy metals in sediment at R6 station



Figure 11. Speciation of heavy metals in sediment at R7 station











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