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TRACE METAL SPECIATION IN ENVIRONMENTAL AQUATIC SAMPLES OF PALAR RIVER, MAHABALIPURM AND ITS ADJOINING COAST

M R KUPPUSAMY+ AND V V GIRIDHAR*

* *Marine Electrochemistry Section, Central Electrochemical Research Institute-Madras Unit CSIR Madras Complex, Taramani, Chennai - 600 113, India*

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Surface waters from 6 stations of riverine and coastal waters of Palar river, Mahabalipurm were collected. The hydrographic parameters for these samples were determined by conventional techniques. The DPASV technique was used for the determination of various forms of trace metals like Zn, Pb, Cu and Cd. The total dissolved metals were determined after UV-irradiation of the 0.45 μ filtered water samples. The ASV labile metals in the filtered water samples were determined at natural pH. The suspended particulate matter retained on the 0.45 μfilter paper were digested by using strong acids and the same were used for the determination of suspended particulate bound metals. The total dissolved metals were in general high at the riverine stations compared to coastal stations. However, last two stations on the seaside were showing higher values relative to the station close to the mixing zone. It was found that the percentages of ASV labile and non-labile forms varied widely with respect to the season at different stations. The particulate Zn, Pb and Cu were showing higher values in the monsoon season in riverine waters and in the summer/pre-monsoon for coastal waters. The higher values of the metals in the riverine side and last two stations on the seaside indicate trace metal pollution in the transect.

Keywords: Trace metals, chemical forms, speciation, labile, non- labile, riverine,coastal waters.

INTRODUCTION

It is well known that organic complexation dominates the chemical speciation of many dissolved trace metals in seawater, thereby regulating their availability to the biota [1-3]. Further, a continuum of metal complexing ligands both of organic and inorganic types of various sizes is known to exist in marine waters spanning from truly soluble to colloidal, the nature of which differs for individual bioactive metals. These ligands play a vital role in the transportation behaviour of trace metals in various components of marine waters. A study on the distribution of metal speciation in coastal environmental systems such as Palar river and their adjoining coastal waters will give an insight into the understanding the various physicochemical processes taking place in these systems and also throw some light on the trace metal pollution. In the present study we aim at discriminating the trace metals present in surface water samples of this eco-system as labile, non-labile and particulate forms. Both riverine and coastal waters have been analyzed for the presence of the above three forms of trace metals with specific reference to Zn, Pb, Cu and Cd. Although there are large number of studies [4-12] dealing with trace metal pollution in Indian estuaries and their adjoining coastal waters both with respect to aqueous phase and sediment phase, very little work has been carried out from the metal ion speciation angle [13-16].

In the present investigation, the trace metal speciation of Zn, Pb, Cu and Cd in the riverine and coastal waters of Palar river, Mahabalipuram transect has been studied by using DPASV technique. This is because it has been well established that electrochemical techniques have an edge over other conventional techniques

+ Author for correspondence. Project Scientist, NIOT, Chennai

especially for studying the speciation of trace metals in aquatic systems [17].

EXPERIMENTAL

Description of the study area

Palar river is one of the major rivers in Tamil Nadu that runs perpendicular to the coast and located 70km south of Chennai. It joins the sea between east of Maduranthakam and south of Kalpakkam near Mahabalipuram. It brings effluents both domestic and industrial during monsoon time from a number of urban settlements and industries situated on its bank. The adjoining coast receives additional effluents from Edaiyur-Sadras backwaters and Buckingham canal, which runs parallel to the coast and join the backwaters in a number of places. The release of pesticides and fertilizers by agricultural practice, the release of municipal sewage due to urban settlement at Kalpakkam (because of the nearby nuclear power station) and Mahabalipuram (because of tourist activities) and salt panning industry are some more causes of environmental concern. In addition, the effluents generated from the nuclear power plant at Kalpakkam adds a new dimension to the coastal pollution along this coast.

The sampling was carried out during Summer (May), Pre-monsoon (September) and Monsoon (December) of the year 1999 along Palar river transect consisting of 3 stations inside the Palar river (using fiber glass boat) and three stations towards seaside (using CRV 'Sagar Purvi') (Fig. 1a). The season is with respect to Northeast monsoon.

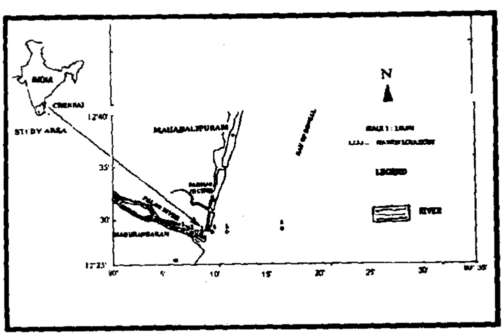

Fig. 1a: Sampling locations for Palar river, Mahabalipuram and its adjoining coast

Surface water samples were collected using a clean plastic bucket and transferred into 2.5 liters acid-washed and pre-cleaned containers. The surficial sediment samples were collected by using a Van veen grab and transferred into pre-cleaned plastic bags. Both the water samples and sediments were stored in frozen conditions. The geographical positions of all estuarine and coastal stations were noted by using a GPS.

The hydrographic parameters water temperature, *p*H, Salinity, Suspended Solids,Dissolved Oxygen and nutrients like ammonia-N, Nitrate-N and Inorganic Reactive Phosphate-P were determined using standard methods [18].

For trace metal determination, initially, the seawater samples collected from the site were filtered a) on board (for coastal samples) and b) as soon as they were brought to the shore laboratory (for estuarine samples)} through a pre-weighed acid washed 0.45 μm pore size HA type Millipore filter paper. The filtrates were stored at 277 K in pre-cleaned 1litre bottles. The total dissolved trace metals, labile and non-labile trace metals were determined by DPASV as per the analytical procedure shown in Fig. 1b and the detailed procedure given elsewhere [19]. The stripping peaks for these metals occurred around -1.1 V (Zn), - 0.7 V (Cd), -0.5 V (Pb) and -0.1 V (Cu). The chemical speciation in this study is restricted to the labile and non-labile discrimination in the dissolved phase.

The suspended particulate matter alongwith the filter papers were stored in petri dishes and packed in plastic bags. After bringing it to room

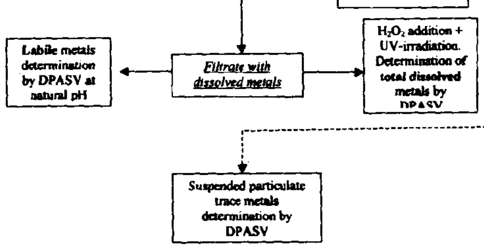

Fig. 1b: Scheme showing the analytical procedure for determination of speciation of trace metals in riverine nd coastal waters of Palar river, Mahabalipuram transect

TABLE I: Average values of geeral wate rquality parameters along different stations of Palar river transect near Mahabalipuram during the study period (The values in the parenthesis is the standard deviation)

Station code	Water temp (K)	Salinity (ppt)	Dissolved oxygen ($mg.l^{-1}$)	*p*H	Suspended solids ($mg.l^{-1}$)	Ammonia nitrogen ($\mu\ mol.l^{-1}$)	Nitrate nitrogen ($\mu\ mol.l^{-1}$)	Inorganic reacrtive phosphate ($\mu\ mol.l^{-1}$)
RMBM1	27.17	15.04	5.84	7.93	25.72	2.12	1.46	0.79
	(1.050)	(16.910)	(1.819)	(0.400)	(8.909)	(1.862)	(2.227)	(0.250)
RMBM2	27.07	15.85	6.04	7.93	24.68	2.00	1.08	1.35
	(1.102)	(16.032)	(1.938)	(0.276)	(6.835)	(1.095)	(1.313)	(0.437)
RMBM3	27.33	21.12	6.28	7.87	28.00	1.38	2.04	1.30
	(0.702)	(15.260)	(1.816)	(0.285)	(2.003)	(0.901)	(2.016)	(0.235)
MBM1	27.33	31.57	6.53	7.86	26.59	2.99	5.51	1.15
	(0.577)	(3.534)	(1.688)	(0.192)	(14.109)	(1.500)	(4.006)	(0.641)
MBM2	27.17	31.72	7.22	7.98	14.70	3.70	3.51	0.90
	(0.289)	(3.185)	(2.374)	(0.032)	(9.712)	(1.945)	(3.814)	(0.546)
MBM3	27.47	31.83	7.7	8.00	6.20	4.48	4.68	0.64
	(0.503)	(2.857)	(3.730)	(0.064)	(5.062)	(0.792)	(2.154)	(0.420)

temperature they were dried at 353 K in an oven for a day. After noting the final weight, the suspended particulate matter bound trace metals were analyzed by DPASV following the procedure of De Luca Rebello et al [20].

RESULTS AND DISCUSSION

The average values of general hydrographic parameters such as water temperature, *p*H, salinity, suspended solids, dissolved oxygen and nutrients are presented in Table I. In general, the average values of parameters like salinity, *p*H, DO and nitrogenous nutrients increased towards seaside, while those of suspended solids and IRP (to some extent) decreased towards coastal stations. Coming to the seasonal variation, the parameters water temperature and *p*H varied very narrowly in both riverine and coastal stations (as indicated by the standard deviation values at each station). However, parameters like suspended solids, dissolved oxygen and nutrients varied over a wide range again with respect to season, now the variation being larger especially in coastal stations compared to riverine stations. On the otherhand, salinity showed larger variation in riverine stations compared to offshore stations.

The total dissolved trace metal concentrations varied from 13.67 $\mu g.l^{-1}$ to 78.38 $\mu g.l^{-1}$ for Zinc, ND to 283.5 $\mu g.l^{-1}$ for lead, 3.68 to 36.7 $\mu g.l^{-1}$ for Cu and ND to 9.49 $\mu g.l^{-1}$ for Cd during the entire study period. These ranges were similar to that noticed at Ennore transect [21]. The highest values of Zn, Pb and Cu were noted in the estuarine stations especially during summer/pre-monsoon. The lower values were found during monsoon season for these elements primarily because of dilution effect. Among the finite values of Cd, higher values were noticed in coastal stations compared to riverine stations. No clear-cut seasonal variation was observed for this element.

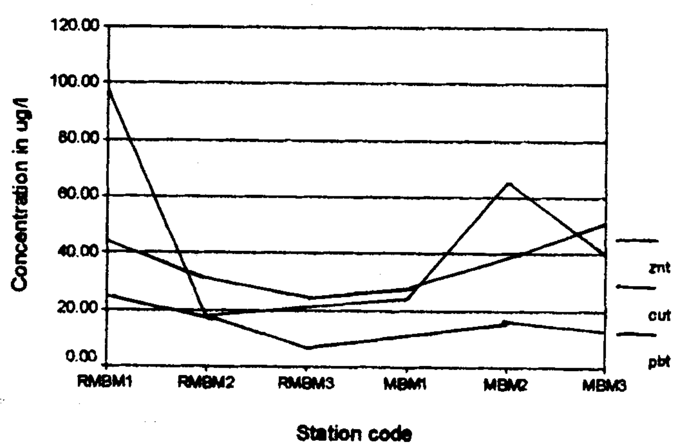

Fig. 2: Variation of average dissolved trace metals concentration along Palar, Mahabalipuram coast

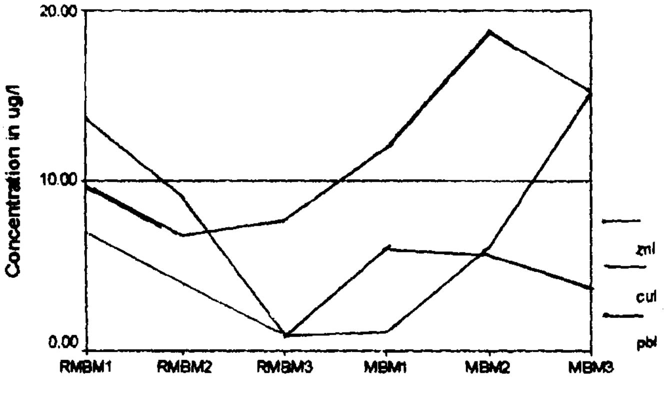

Fig. 3: Variation of average concentrations of labile trace mertals along Palar, Mahabalipuram coast

The variation in the percentages of total dissolved, labile and non-labile forms of different trace metals studied are shown in Figs. 2-4. In general, there was a decreasing trend of dissolved trace metals as one moved from estuarine stations to coastal stations upto nearshore station on the seaside and thereafter increased. However, total dissolved Pb and Cu showed a decrease in the last station MBM3. The non-labile trace metals concentrations also approximately followed the trend of dissolved trace metals. On the otherhand, there was a decreasing trend in labile metal concentrations from RMBM 1 to RMBM 3 and thereafter increased towards coastal stations. A maxima was observed for certain dissolved, non-labile and labile forms of the three trace metals Zn, Pb and Cu at MBM2.

The percentages of various forms of the metals are given in Table II. The data pertaining to Cd has not been included in this table as the total dissolved concentration of Cd in many cases, especially coastal stations, were ND values and it was hence not possible to split it into labile and non-labile forms.

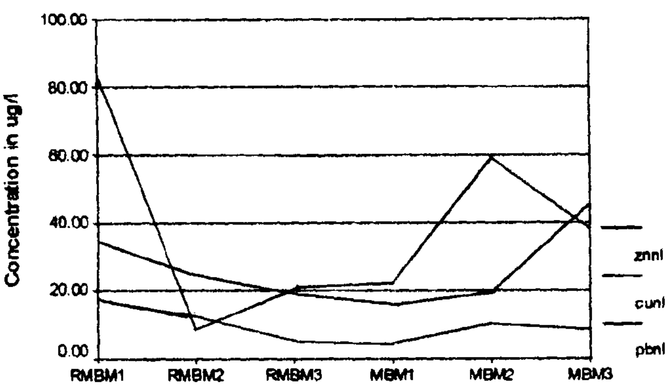

Fig. 4: Variation of average concentrations of non-labile trace metals along Palar, Mahabalipuram coast

The labile form of Zn varied from 3.32% to 53.55% (Table II) during the entire period of study. On the whole, the average % of labile form of Zn was < 50% at most of the stations. A similar percentage (11.3%, 19.0% and 45.0%) of labile form of Zn was noticed by Florence et al in their study in creek water, seawater and Marina waters respectively [22]. The non-labile form of Zinc on the otherhand, varied from 46.45% to 96.68%. However, the average % of non-labile Zn was mostly > 50%. The dominance of % of non-labile form of Zn indicated that the organic effluents containing chelating ligands were brought to the Palar River through land-based run-off.

The labile form of Cu varied from 0.00% to 74.18% during the entire period of study. On the whole, the average % of labile form of Cu was < 50% at all the stations except MBM 1. The non- labile form of Cu on the otherhand, varied from 25.82% to 100.00%.. The average % of non-labile Cu was > 50% at all stations except MBM 1. This indicated domination of non-labile form of Cu at this transect except at MBM 1, where labile form dominated.

The labile form of Pb varied from 0.00% to 65.53% during the study period. The average % of labile form of Pb was < 50% at all the stations. The non-labile form of Pb on the otherhand, varied from 34.47% to 100.00%. However, the average % of non-labile Pb was mostly > 55%. This indicated domination of non-labile form of Pb at this transect during the period of study. However, in their study along Khandla-Porbander shelf region, Bipra Gorai [23] have obtained a higher percentage of labile lead compared to non-labile lead.

These results indicated a considerable amount of seasonal variability of the labile and non-labile forms of the trace metals Zn, Cu and Pb along the Palar river transect during the study period and that the percentage non-labile forms of Zn, Cu and Pb dominated the speciation of trace

TABLE II: Ranges and averages of percentage labile and non-labile forms of different trace metals along different stations of Palar, Mahabalipuram transect

Station code	Range % ZnL	Av % ZnL	Range % ZnNL	Av % ZnNL	Range % CuL	Av % CuL	Range % CuNL	Av % CuNL	Range % PbL	Av % PbL	Range % PbNL	Av % PbNL
RMBM1	3.32-53.55	26.36	46.45-96.68	73.64	21.57-33.33	27.74	66.67-78.43	72.26	12.93-39.85	26.39	60.15-87.07	73.61
RMBM2	9.91-35.23	24.55	64.77-71.48	68.13	0.00-22.36	11.18	77.64-100.00	88.82	0.00-65.53	28.45	34.47-80.18	57.33
RMBM3	12.66-38.95	25.81	87.34-87.34	87.34	0.00-32.91	10.97	67.09-100.00	89.03	0.00-8.24	4.12	91.76-100.00	95.88
MBM1	28.70-50.96	37.78	49.04-71.30	62.22	45.11-74.18	62.93	25.82-54.89	37.07	0.00-14.38	4.79	85.62-100.00	95.21
MBM2	45.18-51.93	47.95	48.07-54.82	52.05	17.07-45.18	28.20	54.82-82.93	71.80	8.47-48.82	28.65	51.18-91.53	71.36
MBM3	8.24-19.32	13.78	80.68-91.76	86.22	19.32-52.32	37.43	47.68-80.68	62.57	3.45-17.96	10.71	82.04-96.55	89.30

metals. The domination of non-labile forms might be due to the release of large amounts of organic effluent flow in to the estuary from municipal sewage and agricultural activities in this area.

Correlation analysis

A bivariate Pearson correlation was made to our data set, which included all the general water quality parameters and percentages of various forms of trace metals using SPSS software version 9.5 with Pearson correlation coefficients as a measure of similarity.

It was found that significant correlations at 0.05 level occurred between water tempe- rature and %PbL (r = -0.511), nitrate-N and % PbL (r = -0.603), silicate-Si and %PbL (r = 0.661) and nitrate-N and %CuL (r = +0.503). No significant correlation occured between general water quality parameters and %ZnL or %ZnNL. further, it was seen that while water temperature and nitrate-N were positively correlated to %PbL that of silicate-Si was negatively correlated. On the other hand, nitrate-N was positively correlated to %CuL.

The ranges of particulate metals alongwith their average values during the study period at different stations are given in Table III. The average values of particulate trace metals were higher in the estuarine stations especially at RMBM 1 for all the trace metals studied except Cd. On the otherhand, in coastal stations, the particulate trace metals showed higher values for Zn and Cd at MBM 2, for Cu at MBM 1 and Pb at MBM 3. Fur- ther, there was a significant negative correlation only for particulate Pb and suspended solids (r=-0.649; n = 18). The overall average values of particulate trace metals over the whole period of study were 124.19 μg/g for Zn, 48.16 μg/g for Cu, 57.89 μg/g for Pb and 1.41 μg/g for Cd. When a closer look at the original data (not shown) was made, it was found that particulate Zn, Pb and Cu have shown higher values during monsooon season compared to summer and pre-monsoon in riverine waters and summer/ pre-monsoon in coastal waters. There was no specific trend for particulate particulate Cd in these waters.

CONCLUSION

A strong seasonal variation of different forms of trace metal speciation was noticed from the present study along Palar river transect, Mahabalipuram. It was found that the non-labile form dominated the speciation of metals in this transect for Zn, Cu and Pb except for Cu in MBM 1 station where the labile form dominated the speciation. The higher values of the metals in the riverine

TABLE III: Ranges and averages of particulate bound forms of different trace metals along different statiosn of Palar, Mahabalipuram tansect

Station code	C.P. zinc (μ . g^{-1})		C.P. copper (μ . g^{-1})		C.P. lead (μ . g^{-1})		C.P. cadmium (μ . g^{-1})	
	Range	Average	Range	Average	Range	Average	Range	Average
RMBM1	126.07-398.39	240.65	0.00-75.91	42.79	0.00-36.54	14.03	ND	ND
RMBM2	0.00-65.44	32.05	20.35-52.5	36.71	0.00-25.2	10.04	0.00-0.29	0.10
RMBM3	41.7-368.67	143.42	0.00-47.25	25.00	0.00-6.55	4.03	ND	ND
MBM1	70.1-224.17	122.76	12.42-326.91	119.20	0.00-40.82	24.37	0.00-4.57	1.52
MBM2	65.0-271.32	169.04	3.79-70.75	29.32	1.51-381.3	141.37	0.00-11.35	3.78
MBM3	24.22-62.07	37.23	0.00-81.75	27.91	9.46-362.16	153.49	0.00-9.22	3.07

C.P. = Concentration of particulate

side and last two stations on the seaside indicated trace metal pollution in this transect.

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