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Distribution of Heavy Metals in Water and Sediments in the Lower Reaches of the Periyar River of Southern Kerala (India)

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KEYWORDS

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A B S T R A C T

The distribution of heavy metals (Cd, Cu, Pb, Zn and Cr) in water and sediment of the River Periyar, a highly polluted river in Southern Kerala (India) has been studied. The river is polluted by municipal, industrial and agricultural effluents, and it flows through the city of Thrissur, Ernakulam and Idukki districts. Water and sediment samples were collected from the lower reaches of the Periyar river. Heavy metal concentration in water and sediment showed significant variation between stations. All the heavy metal concentration in water and sediment was above the permissible limit. Concentration of lead and zinc concentration was high compared to that of other metals. In certain cases chromium concentration was below detectable levels. Higher metal concentration in water and sediments during postmonsoon season established the fact that monsoon had a great effect on status of metals in water and sediments by causing remobilization of metals.

Introduction

In recent years, the influx of heavy metals from terrestrial and atmospheric sources to the aquatic environment has increased considerably (Fostner and Wittman, 1981). Numerous studies have demonstrated that the metal concentrations in sediments gives more sensitive results than that of dissolved in water (Luoma, 1990). The presence of heavy metals in sediments is affected by the particle size and composition of sediments (Filgueiras *et al.*, 2004; Yu *et al.*, 2001). Throughout the hydrological cycle, far less than 1% of pollutants remain dissolved in water whereas over 99% are stored in sediments which therefore are the major sinks and carriers for contaminants in aquatic environments (Filgueiras *et al.*, 2004). A variety of factors such as basin geology, physiography, chemical reactivity, lithology, mineralogy, hydrology, vegetation, land use pattern, pollution and biological productivity regulate the metal load of a river system (Jain, 2001). The relative mobility of metals during transport processes and the historical development of various hydrological and chemical parameters.

The River Periyar is the longest river of the Kerala State. Heavy metal distribution in the Periyar river water was high because of natural and anthropogenic activities. The disposal of untreated and partially treated effluents containing toxic metals, as well as metal chelates from different industries and the indiscriminate use of heavy metals containing fertilizers and pesticides in agricultural fields are the major contributors to accumulation of heavy metals in the Periyar River (Amman *et al.,* 2002).

Rivers in urban areas such as Periyar river have also been associated with water quality problems because of the practice of discharging untreated domestic waste and industrial waste into the water bodies which leads to an increase in the level of metal concentration in river (Venugopal, 2009).

Sediment plays an important role in the transport of nutrients, metals and other contaminants through river systems to the World's Oceans and Seas. Sediments also act as metal reservoirs, the primary exchange models being adsorption or precipitation, and can also provide a reasonably accurate history of pollution in the river (Filgueiras *et al.,* 2004).

Sediment associated metals can be released into the water column and accumulate in plants and animals, thus entering the food web. Sediment may become a source of metals when the environmental conditions (such as pH, redox potential, bioturbation, organic matter decay rate etc.) change in the overlying water (Izquierdo *et al.,* 1997; Klavins *et al.,* 2000).

(Priju and Narayana, 2007) have observed that the heavy metal concentration due to anthropogenic contamination in the Periyar is higher than that of other Indian rivers. A large amount of effluents come from the industries viz., Fertilizers and Chemicals Travancore Ltd (FACT), Hindustan Insecticides, Indian Rare Earths, Travancore Cochin Chemicals (TCC), Cochin Refineries Ltd and Zinc-Alumina ore smelting (Hindustan Zinc and Indian Aluminium Company). About 260 million m3 of effluents are being discharged into Periyar river daily (Balachandran, 2005).

The aim of this study was to evaluate heavy metal content (Cd, Cu, Pb, Zn and Cr) in water and sediment samples in the lower region of Periyar river. Urban and industrial waste, in addition, as well as unlawful dumping and indiscriminate sand mining activities have highly increased the concentration of pollutants.

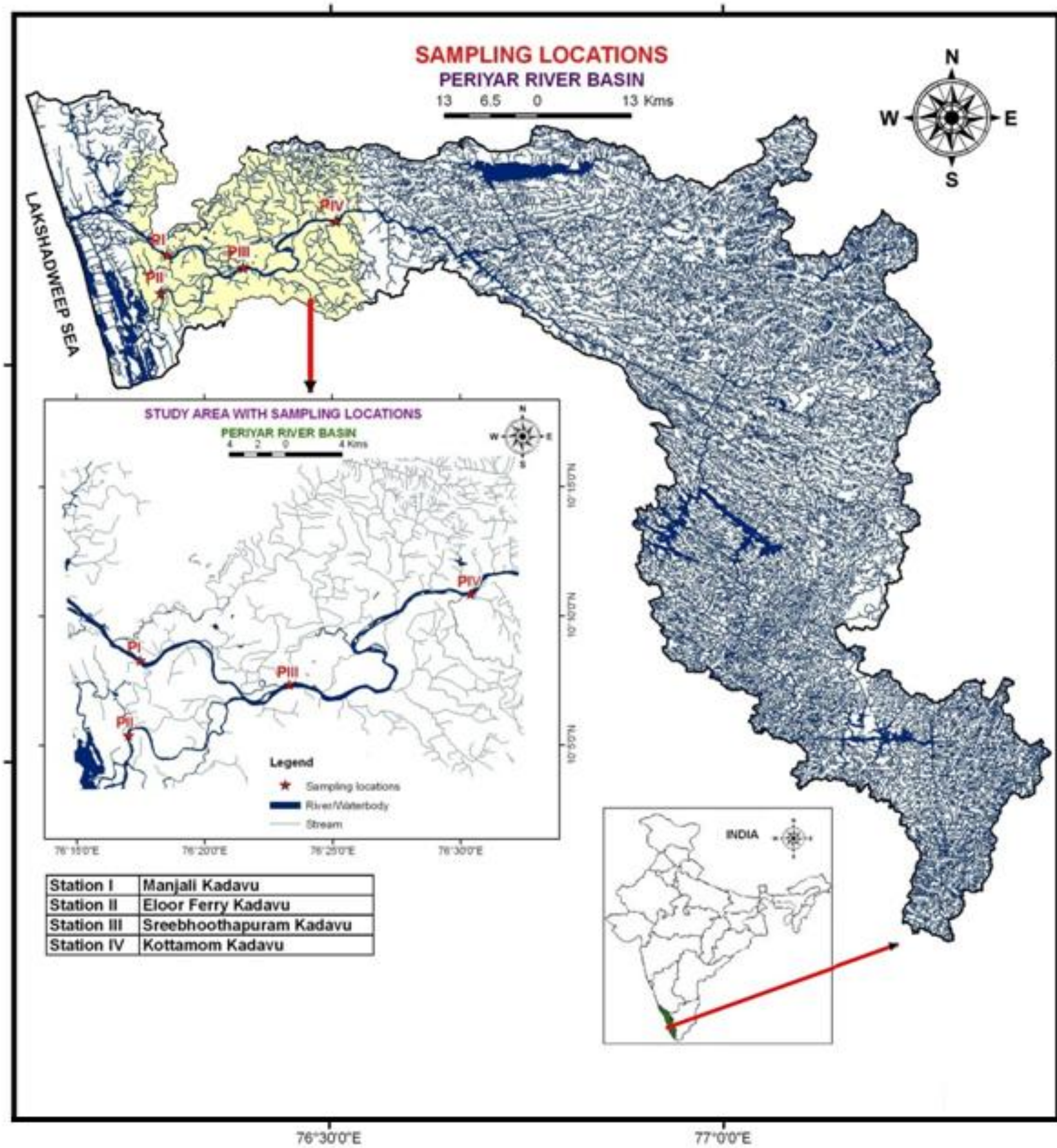
Materials and Methods

Study area

The River Periyar, the longest river of the state is considered to be the life line of central Kerala. It originates in the 'Sivagiri' group of hills in 'Sundaramalai' at an elevation of about 1830m above MSL and flows through highly varied geologic and geomorphic features. After about 48Km it receives the Mullayar and then turns west to flow into the Periyar lake at Thekkady.

The total length is about 300Kms (244 Kms in Kerala) with a catchment area of 5396Sq.Kms (5284 Sq.Kms in Kerala). The total annual flow is estimated to be 11607 Cubic meters. The river has a maximum width of 405m and is located between latitude 9°15'50" and longitude 76°7'38". During its journey to Arabian Sea of Cochin, the river is enriched with water of minor tributaries like *Muthayar*, *Perunthurayar*, *Chinnar*, *Cheruthony*, *Kattapanayar* and *Edamalayar* at different junctures.

Fig.1 Map of the periyar river showing sampling stations



Sample collection and preparation

Fig. 1 shows the 4 sites selected for sampling: PI Manjali *kadavu* (downstream region of the river, 12 Km away from river mouth, near agricultural fields); PII Eloor ferry *kadavu*, (downstream region of the river and near industrial area); PIII Sreebhoothapuram *kadavu*, (upstream confluence of study site and sand mining area) and PIV Kottamom *kadavu*, (upstream confluence of study site and agricultural area).

Sampling design and analytical procedure

From January 2009 to December 2009, water and sediment samples were collected from the Periyar river at lower reaches. The water samples were collected in polythene bottles. The sample bottles were soaked in 10% HNO_3 for 24h and rinsed several times with deionized water prior to use. The sample thus preserved were stored 4°C in sampling kits and brought to the laboratory for heavy metal analysis.

Sediment samples were collected by an Ekman grab sampler, dried 70°C and sieved to obtain different particle fractions (0-75, 75-150, 150-200, 200-250, 250-300, 300-425 and 425-600µm) and stored in polythene bags until further processing. The extraction of sediments was carried out using acid mixture (HNO_3+$HClO_4$). After digestion the solutions were diluted by deionized water. All chemicals and standard solutions used in the study were obtained from Merck, India/Germany and were of analytical grade. Deionized water was used throughout the study. All glassware and other containers were thoroughly cleaned and finally rinsed with deionized water several times prior to use.

Heavy metal analysis was carried out using a Perkin Elmer Atomic Absorption Spectrometer (Model 3110). The metal standards prepared were checked with standard reference material obtained from APHA (2005). Average values of five replicates were taken for each determination. The precision of the analytical procedures, expressed as ANOVA (Analysis of Variance) was at 5% of significant level.

Results and Discussion

3.1 Heavy metal concentrations in water

Considering the importance of heavy metal estimation in pollution assessment study, in recent years, there has been a great spurt of renewed activity to identify the sources and sinks of these metals in various aquatic environments. The fate of heavy metals in river, lakes and near shore environment is of the extreme importance due to their impact on aquatic life at elevated concentrations (Yu *et al.*, 2001; Jain *et al.*, 2008). Monthly and annual distributions of heavy metal concentrations are given in table 1. The lower concentration in dissolved metals in the months of March/April is due to the absence of substantial amount of contaminants from the nearby agricultural and industrial area. The concentration of dissolved metals decreased in the premonsoon months and increased to high concentration during postmonsoon months. It may be attributed to the rainfall, monsoon floods and land drainage etc. which brings large volume of water with heavy metals, both in dissolved as well as associated form into the river. Similar reports were also made by Singh *et al.* (2005) in the Gomti River and Zhang *et al.* (2010) in the Pearl River, China. Regarding annual variation it was evident that higher concentration of cadmium, lead and chromium was noticed at PII. It might be due to the disposal of untreated effluents from industries located on the bank of Periyar river mainly smelting and mining industry (Binani Zinc limited), fertilizing factories, Travancore Cochin Chemicals and Indian Rare Earth Limited. Higher concentration of copper and zinc was noticed at PI and PIV. The reason may be due to the fertilizers and pesticide effluents from the agricultural areas. The order of incidence of total heavy metal concentration in water sample was Pb>Zn>Cu>Cd> Cr. Metal concentration was compared against water quality guidelines (or standards) for drinking water (USEPA, 2004; WHO, 2004) and the protection of aquatic life (USEPA, 2006). The concentration of Cd, Cu, Pb, Zn and Cr at all sites were above or close to the maximum permitted concentration level for drinking water quality guidelines (USEPA, 2009). It was determined that the metal concentrations of all water samples were higher than the maximum permitted concentration level for protection of aquatic life. The dissolved heavy metal concentration at the first two sites situated downstream region of the river contained high amount of Cd, Cu, Pb and Cr which could be attributed to the untreated effluents from the industry as we had already assumed but the high concentration of Zn at PIV may be due to effect of fertilizers and pesticides used in the agricultural areas. Comparison of metal concentration data of the Periyar River reveals that the river water is polluted with heavy metals. The extent of metal pollution in the Periyar river was much more serious than that in any other river system in Kerala.

ANOVA test computed the metals at different sites (Table 2, 3, 4 & 5). The test indicates that all the heavy metals showed significant variation between the stations. It reveals that different stations are capable of accumulating metals differently. Present observation is in conformity with the findings of Caeiro *et al.* (2005).

Table.1 Monthly and annual variations of heavy metal concentration of water in lower reach of Periyar River during 2009

					STATION I									
	(mg/l)	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.38	0.24	0.18	0.20	1.80	1.60	1.20	0.65	0.78	0.86	1.0	0.98	1.33
2	Copper	0.75	0.65	0.60	0.32	3.92	4.6	0.20	0.34	0.58	0.80	0.40	0.64	1.096
3	Lead	1.79	2.95	3.8	0.40	3.40	6.0	11.4	1.04	1.28	1.60	0.70	0.78	2.48
4	Zinc	2.79	3.28	3.76	1.78	1.60	0.80	5.2	3.10	2.10	2.42	6.82	5.92	3.176
5	Chromium	0.07	0.09	0.06	0.278	0.48	BDL	0.80	1.28	3.10	3.2	0.08	0.09	0.483
							STATION II							
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.02	0.06	0.04	0.20	0.90	1.60	1.20	1.68	1.78	0.86	1.0	1.0	2.079
2	Copper	0.98	0.23	0.14	0.32	0.68	4.6	6.20	2.38	1.82	0.80	0.20	0.60	0.976
3	Lead	6.32	7.60	8.40	6.40	5.68	6.0	11.4	6.50	8.50	9.60	10.0	8.70	5.268
4	Zinc	0.70	0.84	0.64	1.78	1.69	0.80	5.2	6.20	6.12	12.2	18.6	11.2	3.522
5	Chromium	0.60	0.70	0.10	0.278	0.792	0.328	0.80	1.32	2.34	3.20	0.36	2.86	0.722
							STATION III							
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.91	0.78	0.06	0.34	1.20	1.40	1.80	2.10	1.8	1.4	0.16	0.21	1.29
2	Copper	2.13	2.34	4.62	2.06	0.80	0.60	0.20	0.90	1.20	1.0	1.60	1.82	1.023
3	Lead	1.41	1.12	1.22	0.70	3.5	6.4	2.80	3.40	4.80	3.80	6.0	5.40	3.282
4	Zinc	0.97	0.92	1.50	0.72	12.1	14.4	4.0	12.1	11.4	12.2	10.8	9.68	5.062
5	Chromium	0.098	0.0078	0.0008	0.046	0.80	BDL	0.70	0.320	0.280	0.24	0.160	0.82	0.432
											STATION IV			
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.79	0.83	0.14	0.50	0.80	1.60	1.40	1.78	1.84	2.30	3.10	4.18	2.012
2	Copper	0.09	0.09	0.02	0.06	0.29	0.20	0.30	0.79	0.96	0.80	0.90	0.98	0.602
3	Lead	0.74	0.63	0.54	0.54	1.84	1.80	1.40	2.51	3.92	3.60	3.80	3.92	2.996
4	Zinc	0.96	0.76	0.72	0.72	2.16	2.34	5.8	3.24	4.98	5.82	6.12	6.83	5.083
5	Chromium	0.080	0.076	0.060	0.060	0.09	0.080	0.60	0.79	0.19	0.20	0.40	0.84	0.385

Table.2 ANOVA comparing heavy metal concentration of water of river in relation to seasons at Station I

	1. Test of univariate models					2. Test of univariate effects				
	Source	TypeIIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	20.794	11	1.89	2.831**	Sides of river	10.098	3	3.366	5.042**
	Error	24.034	36	0.668		Seasons	6.185	2	3.092	4.632**
	Total	44.828	47			Sides of river*seasons	4.511	6	0.752	1.126
Copper	Model	12.522	11	1.138	1.086	Sides of river	2.846	3	0.949	0.905
	Error	37.751	36	1.049		Seasons	3.184	2	1.592	1.518
	Total	50.273	47			Sides of river*seasons	6.492	6	1.082	1.032
Lead	Model	138.152	11	12.559	1.891	Sides of river	35.129	3	11.71	1.763
	Error	239.113	36	6.642		Seasons	71.556	2	35.778	5.387**
	Total	377.265	47			Sides of river*seasons	31.467	6	5.244	0.79
Zinc	Model	190.442	11	17.313	1.793	Sides of river	34.422	3	11.474	1.188
	Error	347.652	36	9.657		Seasons	95.731	2	47.865	4.957**
	Total	538.094	47			Sides of river*seasons	60.289	6	10.048	1.041
Chromium	Model	32.724	11	2.975	1.779	Sides of river	11.978	3	3.993	2.388
	Error	60.198	36	1.672		Seasons	9.857	2	4.928	2.947
	Total	92.921	47			Sides of river*seasons	10.889	6	1.815	1.085

** Significant (p<0.01) * Significant (p<0.05)

Table.3 ANOVA comparing heavy metal concentration of water of river in relation to seasons at Station II

	1. Test of univariate models					2. Test of univariate effects				
	Source	Type IIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	60.82	11	5.529	10.995**	Sides of river	43.929	3	14.463	29.119**
	Error	18.104	36	0.503		Seasons	11.179	2	5.589	11.115**
	Total	78.923	47			Sides of river*seasons	5.172	6	0.952	1.893
Copper	Model	36.814	11	3.347	8.505**	Sides of river	7.433	3	2.478	6.297**
	Error	14.166	36	0.393		Seasons	6.905	2	3.452	8.774**
	Total	50.98	47			Sides of river*seasons	22.476	6	3.746	9.520**
Lead	Model	318.579	11	28.962	12.765**	Sides of river	301.484	3	100.495	44.294**
	Error	81.677	36	2.269		Seasons	14.146	2	7.073	3.117*
	Total	400.256	47			Sides of river*seasons	2.949	6	0.491	0.217
Zinc	Model	343.13	11	31.194	4.084**	Sides of river	147.384	3	49.128	6.431**
	Error	274.994	36	7.639		Seasons	55.373	2	27.687	3.625*
	Total	618.123	47			Sides of river*seasons	140.372	6	23.395	3.063**
Chromium	Model	10.919	11	0.993	1.499	Sides of river	4.504	3	1.501	2.266
	Error	23.846	36	0.662		Seasons	3.935	2	1.968	2.971
	Total	34.766	47			Sides of river*seasons	2.48	6	0.413	0.624

** Significant (p<0.01) * Significant (p<0.05)

Table.4 ANOVA comparing heavy metal concentration of water of river in relation to seasons at Station III

	1. Test of univariate models					2. Test of univariate effects				
	Source	Type IIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	19.536	11	1.776	4.521**	Sides of river	3.469	3	1.156	2.944*
	Error	14.141	36	0.393		Seasons	10.447	2	5.223	13.298**
	Total	33.677	47			Sides of river*seasons	5.62	6	0.937	2.385*
Copper	Model	17.725	11	1.611	3.902**	Sides of river	7.566	3	2.522	6.108**
	Error	14.865	36	0.413		Seasons	0.928	2	0.464	1.123
	Total	32.591	47			Sides of river*seasons	9.232	6	1.539	3.726**
Lead	Model	176.093	11	16.008	4.156**	Sides of river	50.785	3	16.928	4.395**
	Error	138.669	36	3.852		Seasons	108.723	2	54.361	14.113**
	Total	314.761	47			Sides of river*seasons	16.584	6	2.764	0.718
Zinc	Model	374.273	11	34.025	2.949**	Sides of river	117.968	3	39.323	3.408*
	Error	415.403	36	11.539		Seasons	212.447	2	106.224	9.206**
	Total	789.676	47			Sides of river*seasons	43.858	6	7.31	0.633
Chromium	Model	11.953	11	1.087	2.146*	Sides of river	2.632	3	0.877	1.733
	Error	18.229	36	0.506		Seasons	3.265	2	1.632	3.224*
	Total	30.182	47			Sides of river*seasons	6.056	6	1.009	1.993

** Significant (p<0.01) * Significant (p<0.05)

Table.5 ANOVA comparing heavy metal concentration of water of river in relation to seasons at Station IV

	1. Test of univariate models					2. Test of univariate effects				
	Source	Type IIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	42.429	11	3.857	3.282**	Sides of river	6.083	3	2.028	1.725
	Error	42.313	36	1.175		Seasons	32.504	2	16.252	13.827**
	Total	84.742	47			Sides of river*seasons	3.842	6	0.64	0.545
Copper	Model	4.308	11	0.392	3.280**	Sides of river	2.166	3	0.722	6.046**
	Error	4.299	36	0.119		Seasons	1.675	2	0.837	7.013**
	Total	8.607	47			Sides of river*seasons	0.467	6	0.078	0.652
Lead	Model	118.815	11	10.801	3.348**	Sides of river	33.209	3	11.07	3.431*
	Error	116.161	36	3.227		Seasons	49.957	2	24.978	7.741**
	Total	234.976	47			Sides of river*seasons	35.65	6	5.942	1.841
Zinc	Model	419.267	11	38.115	4.191**	Sides of river	73.853	3	24.618	2.707
	Error	327.432	36	9.095		Seasons	295.96	2	147.98	16.270**
	Total	746.699	47			Sides of river*seasons	49.957	6	8.242	0.906
Chromium	Model	4.316	11	0.392	6.164**	Sides of river	2.474	3	0.825	12.956**
	Error	18.229	36	0.506		Seasons	3.265	2	1.632	3.224*
	Total	30.182	47			Sides of river*seasons	6.056	6	1.009	1.993

** Significant (p<0.01) * Significant (p<0.05)

Heavy metal concentrations in sediments

As shown in table 6 concentration of heavy metals at PII situated downstream region was much higher than that at PIII and PIV situated upstream region of the river. Total metal concentration followed the order of PII>PI>PIV>PIII. It was reported that waste water containing high concentration of Cu, Zn and Pb has been discharged into the Periyar river by the effluents from FACT, Indian Rare Earth Limited and Travancore Cochin Chemicals. Monthly distribution of heavy metals in sediments indicates that the metal concentrations increased in the postmonsoon months and decreased in premonsoon months. The same results are reported by Joseph (2002) in the Chithrapuzha River and Prasanth (2009) in the Periyar river. During postmonsoon season, polluted particles (especially fine fraction) are supposed to form layers, and, thus, their distribution in the surface sediment is expected to become similar to effluent dilution or dispersion in the water of the river. The heavy metals get a residence time in water and deposit themselves into sediments. Similar findings are also reported by Jain and Sharma (2001).

The concentration of heavy metals in sediments was found considerably lower than that obtained in river water, most of the heavy metals having precipitated and settled as carbonates, oxides and hydroxide bearing sediments. This elevated level indicates higher exposure risks to the discharge of untreated sewage, municipal waste and agrochemical runoff from nearby cities and village directly into the river. Heavy metals showed significant variations in their concentration with respect to habitats. Sediments collected from the lower reaches of Periyar River showed higher concentration of Pb, Zn and Cr, whereas sediments collected from upstream region of the river showed higher concentration of metals like Cd and Cu. The concentration of Pb and Zn was high compared to other metals but the Cr concentration was below the detectable level (BDL) in certain cases. There is large scale industries in the bank of the Periyar River, which can significantly contribute to the heavy metal load, and the presently observed metal accumulation could be due to anthropogenic factors like the effect of pesticide and fertilizer effluents from agricultural areas. Further, concentrations of heavy metals in sediments reflect both logical mineralogy and origin and nature of the sediments (Anu *et al.,* 2009). Cd, Cu, Pb and Cr are extremely stable elements and hence are very toxic to humans and animals (Kashem and Singh, 2001).

It is well established that Cd, Cu, Pb, Zn and Cr showed definite site-wise variation. Sediment samples from PIV contained high amount of Cd and Cu and it may be due to the effluents from Modern rice mill plant located at this site and also due to land based anthropogenic sources including mining, fertilizers and pesticides used in agricultural activities (Ranjan *et al.,* 2008; Zheng *et al.,* 2008) and paint industries (Lin *et al.,* 2002).

High concentration of Pb was noticed at PIII mainly due to the effluents from lead added gasoline used in automotive fuel, and urban runoff. A high concentration of Zn and Cr was noticed at PIII probably due to the effluents from Binani Zinc Ltd. and United Catalysts India Ltd. Binani Zinc Ltd. produces 7000 tonne/year of zinc and United Catalysts India Ltd. produces 655 m^3/day of chromium. These effluents are directly released into the river without any pretreatment. Concentrations of metals analyzed from different station showed significant variation (Tables 7, 8, 9 & 10).

Table.6 Monthly and annual variations of heavy metal concentration of sediment in lower reaches of Periyar river during 2009

		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
STATION I														
1	Cadmium	0.004	0.003	0.004	0.008	0.009	0.009	0.010	0.001	0.001	0.002	0.001	0.005	0.004
2	Copper	0.003	0.003	0.003	0.004	0.004	0.003	0.004	0.003	0.003	0.004	0.004	0.005	0.003
3	Lead	0.06	0.08	0.10	0.126	0.136	0.148	0.016	0.017	0.018	0.019	0.003	0.09	0.047
4	Zinc	0.012	0.143	0.015	0.016	0.016	0.017	0.018	0.015	0.018	0.019	0.057	0.016	0.022
5	Chromium	0.004	0.001	0.001	0.002	0.005	0.007	0.008	0.008	0.009	0.009	0.002	0.006	0.005
STATION II														
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.009	0.001	0.001	0.001	0.001	0.007	0.008	0.008	0.009	0.009	0.01	0.019	0.007
2	Copper	0.002	0.003	0.003	0.005	0.006	0.007	0.009	0.01	0.014	0.012	0.016	0.180	0.016
3	Lead	0.003	0.004	0.004	0.011	0.019	0.018	0.024	0.026	0.39	0.368	0.039	0.041	0.058
4	Zinc	0.041	0.051	0.051	0.007	0.017	0.05	0.099	0.08	0.08	0.1	0.18	0.21	0.476
5	Chromium	0.0001	0.0003	0.0003	0.0006	0.0009	0.001	0.001	0.009	0.019	0.02	0.024	0.025	0.009
STATION III														
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.001	0.001	0.001	0.009	0.01	0.4	0.86	0.92	1.02	1.09	1.1	1.12	0.159
2	Copper	0.003	0.003	0.004	0.006	0.007	0.020	0.04	0.048	0.049	0.051	0.061	0.069	0.014
3	Lead	0.9	0.912	0.914	0.928	0.931	0.948	0.949	0.951	0.962	0.968	0.972	0.976	0.353
4	Zinc	0.01	0.011	0.012	0.014	0.015	0.169	0.17	0.176	0.178	0.181	0.186	0.189	0.065
5	Chromium	0.004	0.005	0.006	0.008	0.008	0.009	0.01	0.016	0.018	0.019	0.02	0.024	0.005
STATION IV														
		JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	ANNUAL
1	Cadmium	0.009	0.008	0.009	0.01	0.09	1.2	0.09	0.06	0.01	0.02	0.09	0.1	0.626
2	Copper	0.001	0.003	0.006	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.076
3	Lead	0.002	0.003	0.009	0.019	0.011	0.012	0.011	0.011	0.01	0.02	0.041	0.056	0.007
4	Zinc	0.001	0.004	0.004	0.019	0.012	0.015	0.014	0.013	0.012	0.015	0.016	0.018	0.289
5	Chromium	0.0004	0.0001	0.0004	0.016	0.011	0.013	0.012	0.011	0.01	0.015	0.016	0.015	0.004

Table.7 ANOVA comparing heavy metal concentration of sediment of river in relation to seasons at Station I

	1.Test of univariate models					2. Test of univariate effects				
	Source	TypeIIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	0	8	0	2.328*	Sides of river	0	2	0	3.515*
	Error	0	27	0		Seasons	0	2	0	4.370*
	Total	0	35			Sides of river*seasons	0	4	0	0.714
Copper	Model	0	8	0	1.728	Sides of river	0	2	0	0.671
	Error	0	27	0		Seasons	0	2	0	2.078
	Total	0	35			Sides of river*seasons	0	4	0	2.081
Lead	Model	0.222	8	0.028	0.959	Sides of river	0.018	2	0.009	0.317
	Error	0.782	27	0.029		Seasons	0.123	2	0.062	2.13
	Total	1.004	35			Sides of river*seasons	0.08	4	0.02	0.694
Zinc	Model	0.008	8	0.001	2.616*	Sides of river	0.002	2	0.001	2.526
	Error	0.01	27	0		Seasons	0.001	2	0.001	1.411
	Total	0.018	35			Sides of river*seasons	0.005	4	0.001	3.264*
Chromium	Model	0	8	0	1.143	Sides of river	0	2	0	0.249
	Error	0	27	0		Seasons	0	2	0	3.106
	Total	0	35			Sides of river*seasons	0	4	0	0.608

** Significant ($p<0.01$) * significant ($p<0.05$)

Table.8 ANOVA comparing heavy metal concentration of sediment of river in relation to seasons at Station II

	1.Test of univariate models					2. Test of univariate effects				
	Source	TypeIIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	0.001	8	0	5.096**	Sides of river	0	2	0	5.794**
	Error	0.001	27	0		Seasons	0.001	2	0	9.780**
	Total	0.002	35			Sides of river*seasons	0	4	0	2.406
Copper	Model	0.32	8	0.04	5.548**	Sides of river	0.174	2	0.087	12.092**
	Error	0.194	27	0.007		Seasons	0.055	2	0.028	3.826*
	Total	0.514	35			Sides of river*seasons	0.09	4	0.023	3.137*
Lead	Model	0.064	8	0.008	2.256*	Sides of river	0.024	2	0.012	3.427*
	Error	0.096	27	0.004		Seasons	0.032	2	0.016	4.480*
	Total	0.16	35			Sides of river*seasons	0.008	4	0.002	0.559
Zinc	Model	20.736	8	2.592	13.851**	Sides of river	11.292	2	5.646	30.171**
	Error	5.052	27	0.187		Seasons	3.597	2	1.799	9.612**
	Total	25.778	35			Sides of river*seasons	5.847	4	1.462	7.811**
Chromium	Model	0.027	8	0.003	1.574	Sides of river	0.007	2	0.003	1.53
	Error	0.059	27	0.002		Seasons	0.008	2	0.004	1.902
	Total	0.086	35			Sides of river*seasons	0.012	4	0.003	1.432

** Significant (p<0.01) * significant (p<0.05)

Table.9 ANOVA comparing heavy metal concentration of sediment of river in relation to seasons at Station III

	1. Test of univariate models					2. Test of univariate effects				
	Source	TypeIIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	3.996	8	0.499	11.833**	Sides of river	2.249	2	1.125	26.643**
	Error	1.14	27	0.042		Seasons	0.622	2	0.311	7.730**
	Total	5.136	35			Sides of river*seasons	1.124	4	0.281	6.659**
Copper	Model	0.009	8	0.001	9.546**	Sides of river	0.005	2	0.003	21.971**
	Error	0.003	27	0		Seasons	0.002	2	0.001	7.004**
	Total	0.012	35			Sides of river*seasons	0.002	4	0.001	4.605**
Lead	Model	6.258	8	0.782	1079.64**	Sides of river	6.235	2	3.118	4302.705**
	Error	0.02	27	0.001		Seasons	0.015	2	0.008	10.507**
	Total	6.278	35			Sides of river*seasons	0.008	4	0.002	2.668*
Zinc	Model	0.092	8	0.011	5.425**	Sides of river	0.028	2	0.014	6.517**
	Error	0.057	27	0.002		Seasons	0.026	2	0.013	6.141**
	Total	0.149	35			Sides of river*seasons	0.038	4	0.01	4.520**
Chromium	Model	0.001	8	0	11.500**	Sides of river	0.001	2	0	36.224**
	Error	0	27	0		Seasons	0	2	0	6.473**
	Total	0.001	35			Sides of river*seasons	0	4	0	1.651

** Significant (p<0.01) * significant (p<0.05)

Table.10 ANOVA comparing heavy metal concentration of sediment of river in relation to season at Station IV

	1. Test of univariate models					2. Test of univariate effects				
	Source	TypeIIISS	DF	Mean sq	F	Source	Type IIISS	DF	Mean sq	F
Cadmium	Model	40.806	8	5.101	17.677**	Sides of river	21.901	2	10.95	37.950**
	Error	7.791	27	0.289		Seasons	7.368	2	3.684	12.767**
	Total	48.597	35			Sides of river*seasons	11.537	4	2.884	9.996**
Copper	Model	0.638	8	0.08	13.023**	Sides of river	0.362	2	0.181	29.557**
	Error	0.165	27	0.006		Seasons	0.098	2	0.049	8.030**
	Total	0.804	35			Sides of river*seasons	0.178	4	0.044	7.253**
Lead	Model	8.832	8	1.104	19.796**	Sides of river	4.9	2	2.45	43.930**
	Error	1.506	27	0.056		Seasons	1.332	2	0.666	11.946**
	Total	10.337	35			Sides of river*seasons	2.6	4	0.65	11.388**
Zinc	Model	9.262	8	1.158	21.956**	Sides of river	5.638	2	2.819	53.464**
	Error	1.424	27	0.053		Seasons	1.222	2	0.611	11.584**
	Total	10.685	35			Sides of river*seasons	2.402	4	0.6	11.388**
Chromium	Model	0.001	8	0	4.302**	Sides of river	0.001	2	0	12.531**
	Error	0.001	27	0		Seasons	0	2	0	2.655
	Total	0.001	35			Sides of river*seasons	0	4	0	1.01

** Significant ($p<0.01$) * significant ($p<0.05$)

The results were interpreted by ANOVA test, which indicates that there was significant variation in the metal concentration in different stations ($p<0.05$). It reveals that each heavy metal concentration varied significantly in different stations under the influence of various environmental factors (Silva *et al.*, 2009).

Conclusion

The major sources of pollution in the Periyar River includes sewage and garbage, agricultural runoff and industrial pollution. The river directly receives civic effluents from the city. The intensive agricultural practice all along the banks and watershed area has been contaminating the river water with huge amount of pesticides and fertilizers especially during surface runoff in the rainy season. Besides, loosening of surface soil and removal of vegetation from catchment area generate problems related to soil erosion and siltation. Industrial pollution poses the most serious threat to the riverine ecosystem in the lower reaches of Periyar River, where a cluster of small and big industries are operating and are continuously discharging wastewater into the river without proper treatment. In the present study the concentration of all the heavy metals was above the allowable limit in water and sediment. Lead and zinc were of high concentration compared to other heavy metals. The result of the present study focuses on the water and sedimental analysis to indicate the nature and extent of pollution in the Periyar River. The pollutant levels recommended by the regulatory agencies are being exceeded. The prevalent tribulations with heavy metals is that they are persistent and they bioaccumulate in the time periods. In addition to posing a threat to various aquatic components in the river, the level of biomagnifications increases when it transfer from one food chain to other. In an area like the lower reaches of the Periyar River, which is known as one of the toxic hot spots of the river, where the lives of people have a higher dependents on the waters surrounding them either by way of fishing or tourism or other related activities, even a small variation in the river surrounding them can cause severe impact of their life. Measures are to be taken to establish an integrated waste treatment or management system in the polluted area of the Periyar River. The system should have a capacity to reduce the waste generation and to convert the waste into useful products.

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