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DETECTION OF THE HEAVY METAL CONCENTRATION OF WATER IN LOWER REACHES OF THE PERIYAR RIVER, KERALA

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Abstract: A study was undertaken to assess the heavy metals concentration of water in the lower reaches of the Periyar river. Heavy metals such as cadmium, copper, lead, zinc and chromium were analyzed monthly during the period from January 2009 to December 2009. The study reveals that all the heavy metal concentration except that of chromium was above the allowable limit. Concentration of lead and zinc concentration was higher than that of other heavy metals such as cadmium, copper and chromium. Considerable attention is needed to maintain the water quality of the Periyar river especially at the lower reaches of the river.

Key words: Heavy metals, Water quality parameters, Pollution, Reverine ecosystem

INTRODUCTION

Nowadays a large number of new chemicals are being released into the aquatic ecosystems and these pollutants are known to harm the ecosystems because of their toxicity and persistence in the environment. About 40 elements enter the aquatic environment as waste due to industrialization and also anthropogenic activities. Among them cadmium, copper, lead, zinc and chromium are well-known metal pollutants in the fresh water ecosystem (Gale *et al*., 2004). The concentration of metals and their actual impact can be greatly modified by the interaction with natural water constituents. Therefore, knowledge of the concentrations of heavy metals is desirable for the estimation of pollution levels in waters and the determination of background values of metal concentrations in corresponding regions. The present area of study is related to the lower reaches of the Periyar river and the period of study was from January 2009 to December 2009. The river receives urban waste water from the Cochin metropolitan city, as well as industrial water discharges, both treated and untreated. The Periyar river is the hot spot because there are 25 major and numerous small scale industries located in this area. So this region of the Periyar river carries pollution load from different industries and urban runoff. Heavy metal analysis of water samples was carried out monthly during the period from January 2009 to December 2009.

MATERIALS AND METHODS

Water samples were collected from lower reaches of the Periyar river having the length about 60 Km (Fig. 1). The four selected stations for the present investigation are Station I-Manjali *kadavu* located 12 Km away from river mouth. It is the master channel of the Periyar river and is the distributary of *Mangalapuzha* branch and joins Chalakkudy river and after that it debouches into Lakshadweep Sea. The water in this area was turbid due to dumping of domestic waste and chicken waste from poultry farm and pesticide effluents from agricultural areas. Cultivation of rubber, banana, and vegetables is noticed on the river bank. Water is used for washing, bathing etc. Station II-Eloor ferry *kadavu* is the distributary of Marthandavarma branch and joins the Arabian Sea through Cochin backwater system. The station was also less transparent due to pollution from 25 major and numerous minor industries. Industries such as those of fertilizers, pesticides, chemicals and allied industries, petroleum refining, heavy metal processing, radioactive mineral processing, rubber processing units etc. This station is situated 9Km away from Cochin backwater system. Station III- Sreebhoothapuram *kadavu* was highly under threat due to indiscriminate sand mining activities and also polluted by plastic, fertilizer and pesticides effluents. It is located 25 Km away from Cochin

Fig. 1. Map of Periyar river showing sampling stations

backwater system. Station IV-Kottamom *kadavu* is a shallow region of comparatively high transparency. It is 56 Km away from the river mouth. The water is used for domestic purposes such as bathing, washing etc. There is a modern rice mill plant on the bank of the river, the industry treats the effluents and disposes them into the nearby river. Sand mining activities are a regular threat in this area. Heavy metal analysis of water sample was followed as per the methods of APHA (2005) by using AAS. The data on the different heavy metals were treated statistically by adopting the methods ANOVA

RESULTS AND DISCUSSIONS

Table 1 and 2 show monthly, seasonal and annual variation of heavy metal concentration in water samples. ANOVA comparing heavy metal concentration in water sample at four different stations was presented in Table 3, 4, 5 and 6. Heavy metal pollution in riverine environment is usually caused by land runoff, mining activities, industrial effluents and anthropogenic inputs. Traces of cadmium, copper, lead, zinc and chromium etc. have been identified deleterious to aquatic ecosystems and human health (Singh *et al.* 2010). Cadmium is a high toxic non-essential metal. As far as the Periyar river is concerned, the major source point is fertilizer-manufacture unit on its banks. In annual variation of high concentration of cadmium was noticed at Station II (2.079 mg/l). It may be due to the effluents from mines and smelter plants. Station II is the industrial

Table 1. Monthly variations of heavy metal concentration of water (mg/l) in lower reaches of Periyar river during 2009

	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC
STATION I												
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
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
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
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
Chromium	0.07	0.09	0.06	0.278	0.48	BDL	0.80	1.28	3.10	3.2	0.08	0.09
STATION II												
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
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
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
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
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
STATION III												
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
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
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
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
Chromium	0.098	0.0078	0.0008	0.046	0.80	BDL	0.70	0.320	0.280	0.24	0.160	0.82
STATION IV												
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
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
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
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
Chromium	0.08	0.076	0.06	0.06	0.09	0.08	0.60	0.79	0.19	0.20	0.40	0.84

belt of Kerala and this area of the river is exposed to unchecked pollution. In seasonal variation it was observed that high values were recorded in monsoon and postmonsoon season. It may be attributed to the formation of chloride complexes, occurring during the mixing of fresh water with sea water and to the desorption of exchangeable metals due to the increasing concentration of major cations. Moore (1991) also has supported this statement. Monthly variation of cadmium content showed that it was high during the months of August and September. Copper is an essential micronutrient which in nature is widely in free state as well as in combined state. The anthropogenic activities by which copper enters water are the process of smelting, mining, industrial effluent discharge, urban runoff and application of fertilizers and fungicides. The concentration of copper in water also depends on environmental factors, salinity, freshwater discharge and suspended solid load (Joseph, 2002). Annual variation of copper content during the present study showed that there was a high level of copper at Station I (1.09 mg/l) which may be due to the disposal of untreated effluents from the industries located on the bank of the Periyar river mainly smelting and mining industry (Binani Zinc Limited), fertilizer units, Travancore Cochin Chemicals, Indian Rare Earths Limited. Monthly and seasonal variation of copper revealed that it was in a fluctuating pattern at all stations. But a high concentration of copper was noticed during monsoon and postmonsoon seasons. It is mainly attributed to rainfall, monsoon floods, land drainage etc. which bring large volume of water with trace metals in dissolved as well as associated form into the river. The quantity of pollutants brought into the river during flooding far exceeds their normal transport through water into the river system (Maya, 2005). Lead is one of the most abundant toxic pollutants in the environment. It becomes a real cause of concern as a contaminant because of its constant and continuous release into air, water and soil in appreciable amounts (Branica, 1980). Annual variation of lead concentration showed that it was wide spread in the study area and it was high at Station II (5.26 mg/l). The high concentration of lead in Station II may be due to the effect of discharge of effluents from the nearby petrochemical industries, fertilizer factories and oil refineries. Studies of Ali *et al.* (2009) and Fotedar and Raina (2009) in Ganga

Table 2. Seasonal and annual variation of heavy metal concentration in water samples (mg/l) in lower reaches of Periyar river during 2009

Station	Cadmium	Copper	Lead	Zinc	Chromium
			PREMONSOON		
I	0.798	0.989	1.307	1.541	0.302
II	1.356	0.458	4.582	1.932	0.27
III	0.673	1.05	1.105	2.272	0.267
IV	0.799	0.321	1.431	1.106	0.093
			MONSOON		
I	1.51	1.615	4.22	3.77	1.053
II	2.523	1.782	5.58	3.611	0.985
III	1.708	0.89	2.94	6.59	0.553
IV	2.55	0.693	3.68	6.36	0.466
			POSTMONSOON		
I	1.685	0.703	1.933	4.23	0.363
II	2.367	0.694	2.76	5.021	0.918
III	1.59	1.129	3.865	6.323	0.478
IV	2.708	0.8	3.893	7.614	0.597
			ANNUAL VARIATION		
I	1.33	1.096	2.48	3.176	0.483
II	2.079	0.976	5.268	3.522	0.722
III	1.29	1.023	3.282	5.062	0.432
IV	2.021	0.602	2.996	5.083	0.385

Table 3. 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	Type III SS	DF	Mean sq	F	Source	Type III SS	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 4. 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	TypeIIISS	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 5. 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	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	3408*
	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 6. 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 III SS	DF	Mean sq	F	Source	Type III SS	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 ($p<0.05$)

river also support these statement. Seasonal variation showed that the highest concentration of lead was in monsoon season except at Station IV. John Kennedy (1999) also observed high concentration of lead during monsoon, which may be due to the mixing of water during rainy season and oil waste from mechanized boats and trawlers, automobile discharges and industrial effluents. Monthly variation of lead showed that the highest concentration was in June and July months. Zinc is one of the most abundant trace elements in the environment. The main pollutant sources of zinc are metalliferous mining activities, ore-dressing and processing of sewage sludge for agricultural use and compost materials and pesticides. In the Periyar river industrial effluents and municipal waste from the city are the main source of zinc. Annual variation of zinc content showed that it was high at Station IV (5.08 mg/l). The high concentration of zinc at Station IV may be due to the action of fertilizers from the agricultural fields and also sand and gravel mining activities. Monthly and seasonal variation of zinc concentration was in a fluctuating pattern. In seasonal variation, a higher concentration was noticed during postmonsoon season. The higher concentration of zinc may be due to land runoff and influx of metal rich freshwater during raining. Similar findings are also reported by Singh (2010) in the Gomti river and Zhang et al. (2010) in the Pearl river, China. Chromium is one of the least toxic of trace elements on the basis of its oversupply and essentiality (Forstner and Wittmann, 1979). Sources of chromium include metal plating, organic and petrochemicals, fertilizers and industrial dyes. The highest concentration of chromium was observed at Station II (0.72 mg/l). The high value of chromium in Station II may be due to the discharge of effluents from various industries such as FACT, petroleum refineries, Travancore Cochin Chemicals, Indian Rare Earth Limited, Cochin refineries and electroplating industries. Chromium exhibited comparatively a lower concentration than other heavy metals. Monthly variation of chromium was in a fluctuating pattern. In seasonal variation a higher concentration was observed during monsoon season, which was mainly due to large runoff and influx of metal- rich fresh water. Concentration of metals analyzed from different stations varied considerably. It was evidenced by the ANOVA test, which indicates that there was a significant variation in metal concentration between the stations ($p<0.05$).

This reveals that different stations are capable of accumulating metals differently. The present observation is in conformity with the findings of Caiero *et al.* (2005).

CONCLUSIONS

The major sources of pollution in the Periyar river include 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 amounts of pesticides and fertilizers especially during surface runoff in the rainy season. Besides, loosening of surface soil and removal of vegetation from catchment area generates 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 study concentration of all the heavy metals in water was above the permissible limit. Concentration of lead and zinc was higher relatively. Concentration of this type of dangerous chemicals should be measured at regular intervals and whenever it reaches above the safe limit, immediate warning has to be issued and suitable steps to be taken to prevent the damage. An environmental monitoring system should be established in the polluted area of the river. The system should have the capability of monitoring water, sediment, aquatic biota and the magnitude of solid and liquid form of industrial effluents.

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