Research Article

Assessing of Water Quality Pollution Indices for Heavy Metal Contamination of Periyar River, Tamil Nadu, South India

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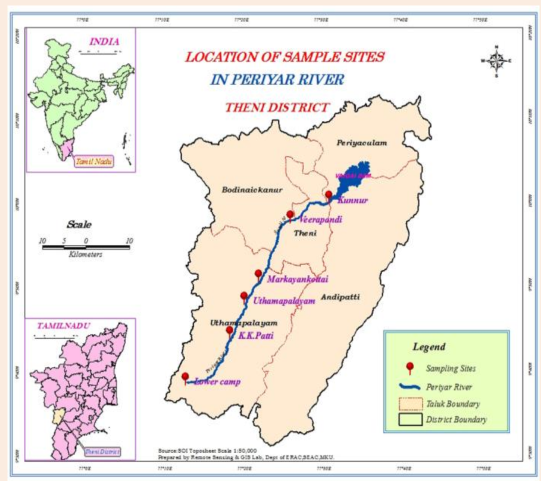
Abstract

The objective of the study is to reveal the water quality of Periyar river with respect to heavy metal contamination. Water samples were collected to find out the extend of metal contamination from six different sampling sites along the 53 km stretch of the Periyar river, Tamil Nadu, South India. The concentrations of metals such as Lithium, Beryllium, Boron, Aluminium, Chromium, Manganese, Iron, Nickel, Cobalt, Copper, Gallium, Selenium, Strontium, Cadmium, Tellurium, Barium, Thallium, Bismuth, Lead and Zinc were determined using Inductively Coupled Plasma Mass-Spectrometry (ICP-MS). The mean values of all the samples were found within the permissible limit of Indian drinking water quality standard (IS: 10500: 2012). The data generated were used to calculate the Contamination Index (C_d), Heavy Metal Evaluation Index (HEI) and Heavy Metal Pollution Index (HPI) of Periyar river. The mean values of HPI values for selected six sampling sites viz., (Lower camp, K.K Patty, Uthamapalayam, Markayankottai, Veerapandi and Kunnur) 16.74, 24.27, 24.61, 26.77, 29.09 and 31.50 respectively, which are below the critical value of 100. Samples from all six sampling sites were classified as low heavy metal contamination using the C_d, and HEI, though overall C_d, HEI and HPI values indicate that the Periyar river, is not critically polluted with respect to these heavy metals. The Statistical analyses were performed to assess the heavy metal pollution load of the Periyar river.



Keywords: Water quality, Heavy metal pollution, Periyar river, Heavy metal pollution index

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Introduction

Rapid urbanization and industrial development during last decade has provoked some serious concerns for the environment. The important anxiety with regards to environmental quality is focused on water because of its significance in monitoring the human health as well as ecosystem health. The chemical composition of water is vital criteria that decide the quality of water [32]. Heavy metal contamination in river is one of the major issues in many fast growing cities, because maintenance of water quality and sanitation infrastructure did not increase along with population and urbanization growth especially for the developing countries [29,5,3]. Heavy metals are among the most common environmental pollutants in water bodies and biota due to natural or anthropogenic sources. The metals are added to the water bodies through natural chemical weathering process and leaching of soil. The anthropogenic sources are associated mainly with industrial and domestic effluents, urban storm water runoff, landfill leachate, mining of coal and ore, atmospheric sources and inputs from rural areas [34,28,8]. Rivers in urban areas have also been associated with water quality problems because of the discharge of wastes from untreated domestic and small scale industries into the water bodies which increase the metal concentration in river water and becomes potentially toxic[31,25,14,2]. Some of these metals are essential as micronutrients in animals and plants while many other metals have no known function [13,30,6]. Metals are non-degradable and causing damage to nervous system and internal organs [14,15]. However, the rivers play a major role in assimilation or transporting municipal and industrial waste water and runoff from agricultural and mining land [27]. The spatial study of heavy metals by producing heavy metal pollution index can be helpful in identifying and quantifying trends in water quality [20,22] and providing tool for better resource management [17].

Periyar River is one of the main sources of water which satisfies the domestic and agricultural needs of the five districts of Tamil Nadu, South India. The adjoining areas of the river are used as sink and repositories to discharge and dispose off industrial (small scale), agriculture and domestic waste, deteriorating the water quality and hence there is a need for a quality assessment of Periyar River. The present study is aimed to investigate the water quality status of Periyar River, with respect to its heavy metal concentrations by preparing the most recent heavy metal evaluation methods.

Materials and Methods

Study Area

Six sampling sites have been fixed at the stretch of 53 km along Periyar river as given in **Figure 1** namely Lower Camp (lat $9^0 38'48.93''$N, long $77^0 12'51.61''$E-upstream), Kamayagoundanpatty (lat $9^0 44'16.91''$N, long $77^0 18'28.93''$E- upstream), Uthamapalayam (lat $9^0 48'22.55''$N, long $77^0 20'17.71''$E-mid stream), Markayankottai (lat $9^0 50'58.07''$N, long $77^0 22'07.16''$E- midstream), Veerapandi (lat $9^0 58'01.03''$N. long $77^0 26'10.46''$E- downstream) , Kunnur (lat $10^0 00'18.43''$N, long $77^0 30'59.50''$E-downstream).

The sites have been selected based on certain features like intensive agricultural activities, discharge of sewage, cloth washing, cattle washing, vehicle washing, agricultural runoff, pilgrim visit etc.,

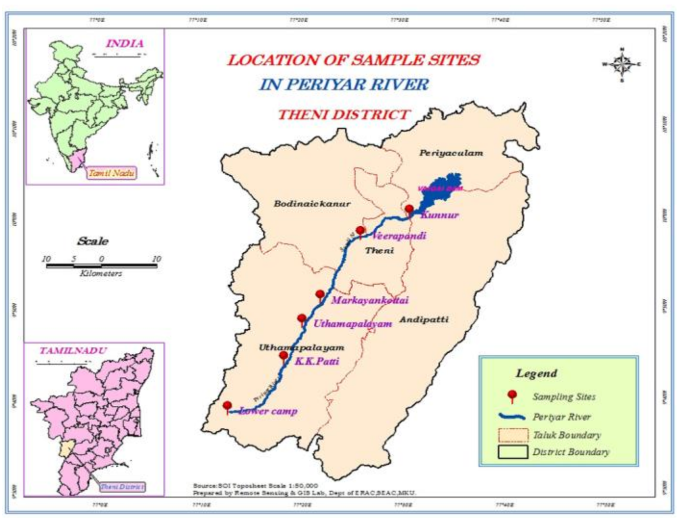

Figure 1 Location of sample sites in Periyar River

Method of Investigation

Field sampling and laboratory methods

The water quality parameters were monitored for a period of one year and six months (January 2012 to June 2013) by taking the samples fortnightly. The samples were collected at 10-15 cm depth in separate pre-conditioned and acid rinsed clean polypropylene bottles. The collected samples were filtered (Whatman no. 42) and acidified with concentrated nitric acid to a pH below 2.0 to minimize precipitation and adsorption on container walls. Heavy metal concentrations (Li, Be, B, Al, Cr, Cd, Co, Cu, Ga, Se, Sr, Te, Ba, Tl, Bi, Fe, Mn, Ni, Pb and Zn) were determined in acidified filtrate water samples by Inductively Coupled Plasma Mass-Spectrometry (ICP-MS). Average values of three replicates were taken for each determination. Appropriate drift blank was taken before the analysis of samples.

Heavy Metal Evaluation Methods

The Contamination Index (C_d)

The contamination index method uses the degree of contamination C_d that calculates the quality of water. It is computed as follows using the equation given below and "it summarizes the combined effects of a number of quality parameters regarded as unsafe to household water" [21].

$$C_d = \sum_{i=1}^{n} Cfi$$

$$Cfi = \frac{CAi}{CNi} - 1$$

Where, Cfi -the contamination factor for the *i*th component
CAi - analytical value for the *i*th component
CNi - upper permissible concentration of the *i*th component
(N denotes the "normative value") [9]. C_d is calculated for every sample independently, values are grouped into three categories regarding contamination level as follows: low contamination if C_d values are lower as one ($C_d<1$), medium contamination when C_d = 1-3, and when C_d is higher as three ($C_d>3$) contamination is high [7].

Heavy Metal Pollution Index

Heavy metal pollution index (HPI) is a technique of rating that provides the composite influence of individual heavy metal on the overall quality of water. The rating is a value between zero and one, reflecting the relative importance of individual quality considerations and inversely proportional to the recommended standard (Si) for each parameter [19, 20, 22].The calculation of HPI involves the following steps:

- First, the calculation of weightage of i^{th} parameter
- Second, the calculation of the quality rating for each of the heavy metal
- Third, the summation of these sub-indices in the overall index

The weightage of i^{th} parameter

$$\mathbf{Wi = k / Si} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(1)}$$

Where, Wi is the unit weightage and Si the recommended standard for i^{th} parameter, while k is the constant of proportionality.

Individual quality rating is given by the expression

$$Qi = 100\, Vi / Si \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Where, Qi is the sub index of i^th^ parameter, Vi is the monitored value of the i^th^ parameter and Si the standard or permissible limit for the i^th^ parameter.

The Heavy Metal Index (HPI) is then calculated as follows

$$HPI = \Sigma^{n}_{i=1}(Qi\, Wi) / \Sigma^{n}_{i=1} Wi \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Where, Qi is the sub index of i^th^ parameter. Wi is the unit weightage for i^th^ parameter, n is the number of parameters considered. The critical pollution index value is 100. For the present study, the Si value is taken from the Indian Standard for drinking water specifications [12].

Heavy Metal Evaluation Index (H_{ei})

This method gives an overall quality with respect to heavy metals, like HEI method, which can be computed with the help of the following equation:

$$HEI = \sum_{i=1}^{n} \frac{Hc}{Hmac}, \quad \text{where}$$

Hc reflects the monitored value of the *i*th indicator and Hmac the maximum admissible concentration of the *i*th parameter. This index is used for a better understanding of the pollution indices.

Statistical Analysis

Results were presented as mean ± SD. The Pearson's correlation analyses, Analysis of Variance (ANOVA) were used for the statistical analyses of results obtained at 95% confidence level using Microsoft Excel 2007 package.

Correlation Coefficient and Linear Regression

Let X and Y are the two variables, and then the correlation coefficient [PEARSON] (r) between the variable X and Y is given by

$$r = \frac{N\sum(X_iY_i) - (\sum X_i).(\sum Y_i)}{\sqrt{[N\sum X_i^2 - (\sum X_i)^2][N\sum Y_i^2 - (\sum Y_i)^2]}}$$

If the values of correlation coefficient 'r' between two variables X and Y are fairly large, it implies that these two variables are highly correlated. In such cases it is fissile to try linear relation in the form

$$Y = a + b\,X$$

The value of empirical parameters '*a*' and '*b*' are calculated with the help of the following equation

$$b = \frac{\Sigma XY - \bar{X}\,\Sigma Y}{\Sigma X^2 - \bar{X}\,\Sigma X}$$

$$a = \bar{Y} - b\,\bar{X}$$

Results and Discussion

Table 1 presents the mean, standard deviation of twenty heavy metals respectively for six different sampling sites of Periyar river, during the study period between January 2012 and June 2013. The metal concentrations were significantly different between sampling locations. However, the concentrations of all heavy metals were found within the permissible value of Indian standards for drinking water quality [12].

Table 1 Quantitative data on selected heavy metals at six sampling sites of Periyar River, Tamil Nadu, South India during the study period from January 2012 to June 2013

S.No	Parameters	Sampling Sites*					
		LC	KKP	UP	MK	VP	KU
1	Lithium (µg/L)	0.330 ±0.10	0.438 ±0.11	0.494 ±0.16	0.512 ±0.10	0.583 ±0.19	0.658 ±0.14
2	Berylium (µg/L)	0.034 ±0.01	0.04 ±0.07	0.052 ±0.03	0.054 ±0.04	0.054 ±0.08	0.123 ±0.19
3	Boron (µg/L)	37.936 ±22.50	42.305 ±11.26	42.541 ±10.77	42.745 ±14.87	43.902 ±16.70	65.408 ±20.65
4	Aluminium (µg/L)	83.221 ±35.88	118.247 ±87.84	122.445 ±140.23	128.081 ±101.14	133.588 ±75.70	101.979 ±110.26
5	Chromium (µg/L)	2.147 ±0.59	2.390 ±0.78	2.478 ±0.78	2 .849 ±0.87	2.859 ±2.09	3.264 ±1.07
6	Manganese (µg/L)	46.158 ±27.43	46.922 ±41.29	37.158 ±36.85	54.308 ±35.09	39.490 ±46.79	57.068 ±130.01
7	Iron (µg/L)	255.635 ±229.53	309.557 ±252.65	318.191 ±240.33	326.730 ±346.11	340.151 ±199.35	418.358 ±617.92
8	Nickel (µg/L)	2.208 ±0.64	2.546 ±1.07	2.633 ±2.64	2.846 ±1.41	3.003 ±1.19	3.773 ±1.98
9	Cobalt (µg/L)	0.604 ±0.48	0.694 ±0.82	0.823 ±0.91	0.849 ±0.79	0.925 ±0.71	0.954 ±1.38
10	Copper (µg/L)	6.942 ±7.31	7.074 ±2.99	7.216 ±3.24	8.126 ±3.00	8.141 ±7.23	8.798 ±2.99
11	Gallium (µg/L)	2.887 ±1.55	6.007 ±1.41	6.443 ±2.11	6.759 ±1.71	7.275 ±2.68	7.739 ±1.58
12	Sellinium (µg/L)	0.289 ±0.08	0.340 ±0.12	0.349 ±0.11	0.523 ±0.29	0.548 ±0.22	0.556 ±0.22
13	Stroncium (µg/L)	128.945 ±100.74	334.474 ±170.23	326.990 ±121.82	370.791 ±116.05	437.927 ±160.27	580.611 ±188.71
14	Cadmium (µg/L)	0.209 ±0.11	0.211 ±0.20	0.253 ±0.13	0.302 ±0.12	0.337 ±0.18	0.414 ±0.30
15	Tellurium (µg/L)	BDL	5.550 ±2.47	6.019 ±2.79	7.161 ±2.81	7.565 ±3.12	7.666 ±4.40
16	Barium (µg/L)	87.626 ±51.16	167.348 ±45.24	179.209 ±56.18	199.356 ±55.74	199.604 ±86.60	214.136 ±62.17
17	Thallium (µg/L)	0.013 ±0.01	0.017 ±0.01	0.024 ±0.02	0.027 ±0.02	0.040 ±0.07	0.065 ±0.09
18	Bismuth (µg/L)	0.287 ±0.36	0.413 ±0.76	0.282 ±0.49	0.265 ±0.24	1.197 ±2.29	1.753 ±3.56
19	Lead (µg/L)	4.971 ±1.69	7.590 ±2.53	7.621 ±3.41	8.139 ±2.44	8.899 ±2.46	9.516 ±2.79
20	Zinc (µg/L)	31.156 ±21.82	48.468 ±34.28	62.692 ±46.23	68.655 ±50.36	73.054 ±52.90	77.733 ±56.38

*Sampling Sites- LC- Lower Camp, KKP- Kamayakoundanpatty, UP- Uthamapalayam, MK- Markayankottai, VP- Veerapandi, KU- Kunnur

Monthly mean values of selected heavy metals during the study period between January 2012 and June 2013 are analyzed to assess the annual variations. In overall view, all selected metals progressively increased in their concentrations in water from upstream sampling sites towards downstream sampling sites. These similar results also observed in Cauvery River [1]. Generally intermediate levels of all metals are recorded at midstream sampling sites. In all metals, maximum mean concentrations were recorded at downstream sampling site Kunnur, while minimum values at upstream sampling site (Lower camp) due to the absence of any major point sources of metal pollution. However, the lowest concentration of metals recorded in the upstream at Lower Camp may be due to natural weathering process of rocks and surface runoff. Similar reasons were projected for the low metal concentration in river Pachin, Arunachal Pradesh, which is also exclusively free from industrial pollution [11] as river Periyar at upstream sampling sites. Generally rivers polluted by non- industrial sources were reported to show low levels of heavy metals in water [26, 33]. However all metals increased at mid stream sampling sites possibly due to : i) increase in non-point sources of pollution and their intensities and ii) continuous transport of metals towards midstream sampling sites by the high rate of river flow at sampling site Lower camp (LC). Land runoff, anthropogenic activities, agricultural runoff and solid wastes dumping are these sources that might have contributed to enhanced levels of metals at midstream sampling sites. These sources were reported to be the reasons for increasing levels of heavy metals in rivers of Andhra Pradesh [33]. At downstream sampling sites, the river is subjected to mild industrial pollution by effluents from small-scale industries viz., printing, steel works industries, electroplating and automobile workshops. In addition to this, there is continuous transport of metals from midstream sampling sites by moderate flow of river. Thus all metals reached their highest levels at downstream sampling sites. Similar to the present results is the annual variation in different heavy metals in water of many rivers already reported [18, 24, 26, 33]. The selected metals reached their highest levels especially at sampling site Kunnur. In addition another major factor is the input of waste from small scale industries in Theni into the river by the tributary, Kottakudi river. The increasing trend of average metal levels was as follows: Tl< Be< Cd< Se< Li< Bi< Co< Cr< Ni< Te< Ga< Cu< Pb< B< Mn< Zn< Al< Ba< Fe< Sr. The results agreed with the EPD report [10] that Zn was the most abundant in the river water, followed by Cu and Pb, and the least was Cd, Cr and Ni. Concentration of all heavy metals is considerably higher in downstream sampling sites than in the other sampling locations. Heavy metal pollution index is an effective tool to characterize the surface water pollution [20, 22] as it combines several parameters to arrive at a particular value which can be compared with the critical value to assess the level of pollution load. In order to calculate the HPI of the water, the mean concentration value of the selected metals (B, Al, Cr, Mn, Fe, Ni, Cu, Se, Cd, Ba, Pb and Zn) have been taken into account**. Table 2** details the standard permissible value (Si) as obtained in the presented study to evaluate the heavy metal pollution. As the mean of heavy metal pollution index value was found to be 25.49 below the critical value of 100, Periyar river is not critically polluted with respect to heavy metals.

HPI was also calculated separately for each sampling location to compare the pollution load and assess the water quality of the selected locations (**Table 3**). The highest value of HPI was found in downstream sampling site (Kunnur.) Heavy metals which were found to have anthropogenic origin and mainly from urban waste, municipal sewage, domestic wastes, traffic sources, atmospheric depositions and chemical weathering of minerals increase their concentration in water [16]. The calculated C_d values are beneath zero, the C_d value for low contamination, with a maximum concentration of -9.197 for downstream sampling site (Kunnur), -10.334 for the minimum value, for upstream sampling site (Lower camp) and the mean of six different sampling sites are -9.592. The HEI values are divided into three classes: low contamination (HEI < 400), medium contamination (HEI = 400-800) and high contamination (HEI > 800) [9]. HEI for Periyar river are beneath 400, a mean of 2.408 with a maximum value of 2.803 (Kunnur) and a minimum value of 1.666 (Lower camp), denotes a fall into the low contamination zone. We can observe that upstream sampling site (Lower camp) has the lowest concentration for all pollution indices (C_d, HPI and HEI) and downstream sampling site (Kunnur) has the highest values for C_d, HPI and HEI.

Table 2 The Permissible values of various Heavy metals for drinking water recommended by the Indian Standards

S.No	Parameters	IS 10500:2012
1	Iron (µg/L)	300 – 1000*
2	Copper (µg/L)	50 – 1500*
3	Manganese (µg/L)	100 – 300*
4	Cadmium (µg/L)	3*
5	Sellinium (µg/L)	10*
6	Lead (µg/L)	10*
7	Zinc (µg/L)	5000 - 15,000*
8	Chromium (µg/L)	50*
9	Aluminium (µg/L)	30 – 200*
10	Boron (µg/L)	500 – 1000*
11	Barium (µg/L)	700*
12	Nickel (µg/L)	20*

*Permissible values of various heavy metals for drinking water (IS 10500:2012)

Table 3 Results of heavy metals Evaluation methods for six different sampling sites for Periyar river, Tamil Nadu, South India, during the study period from January 2012 to June 2013

Sampling Sites*	Heavy metal Evaluation Methods		
	Contamination Index(C_d)	Heavy metal pollution Index(HPI)	Heavy Metal Evaluation Index(HEI)
LC	-10.33	16.74	1.66
KKP	-9.69	24.27	2.31
UP	-9.61	24.61	2.40
MK	-9.44	26.77	2.56
VP	-9.29	29.09	2.71
KU	-9.19	31.50	2.80
Mean	-9.59	25.50	2.41
Minimum	-10.33	16.74	1.66
Maximum	-9.19	31.50	2.80

*Sampling Sites- LC- Lower Camp, KKP- Kamayakoundanpatty, UP- Uthamapalayam, MK- Markayankottai, VP- Veerapandi, KU- Kunnur

Pearson's correlation coefficient between various heavy metals of Periyar river water

Pearson's correlation coefficients of heavy metals studied in the Periyar river water have been summarized in the **Table 4.** Correlation analysis showed positive correlation between Cr-B and Al. Another group represented by Zn- Pb also displayed a significant strong correlation (r = 0.6897, $P < 0.01$). Pb showed a positive correlative with B (r=0.5097) and Ba (r=0.5264) at p< 0.01. Heavy metals showing very high correlation may indicate same source. Al, Mn and Fe showed negative correlation with B, Cu, Se, Cd, Ba. Pb showed negative correlation with Al. Cd, Ba and Pb showed negative correlation with Fe. Se and Ba showed a negative correlation with Mn. Zn also showed positive correlations with Pb (r = 0.6897) at $P < 0.01$ level indicating its relationship with the Fe-Pb-Cd-Cr-Ni-Cu-Se-Al-Mn group. Fe-Pb-Cd-Cr-Ni-Cu-Se-Al-Mn comes mainly from industrial activities/effluents though untreated domestic sewage discharges and traffic sources also contribute to it. Zn-Cu finds its main source from processing units and chemical weathering of the minerals. From the above correlation coefficient, most positive correlated parameters were taken in to account to find the regression equation. The regression equation for some pairs of heavy metals showed in the **Table 5** which have significant value of correlation. Positive correlation can also be attributed to same origin while the metals with negative correlation are an indication of distinctive sources for the metals in the river [4].The significant positive correlations were observed between the heavy metal contents in water i.e the metals in the two environmental media could have common sources. The metals probably originate from either same waste or parent material as the case may be, as pointed out earlier [23].

Conclusion

The present study is an attempt to detect changes in the water quality characteristics within the Periyar river, with respect to heavy metals. The study reveals that there are additions of large quantities of effluents due to movement of fertilizers from agricultural activities sewage discharge and other anthropogenic wastes particularly in the down streams of the river. The increasing trend of average metal levels was Tl< Be< Cd< Se< Li< Bi< Co< Cr< Ni< Te< Ga< Cu< Pb< B< Mn< Zn< Al< Ba< Fe< Sr. The concentrations of all heavy metals were found within the permissible value of Indian standards for drinking water quality [11] because there is no major industries present along the stretch of the Periyar river. The heavy metals present in the six different sampling sites were due to sewage discharge, solid waste, open drainage agricultural run-off and urban run-off. The C_d (<0) place all the samples as low contamination level. The HPI method consider the level of contamination as noncritical (<100). HPI method is a very useful pollution evaluation tool in assessing over all pollution of water bodies with respect to heavy metals [20]. The third method, HEI method, developed during the study gives a pollution classification for the Periyar river water samples which straddle three classes: low, medium and high with more that all the sampling sites have the low class contamination (<400). All metal concentrations do not overage the standard values, observation that reflects the negative results for the pollution indices. Conclusively, the Periyar River, Tamil Nadu, South India is not deteriorated by heavy metal pollution.

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Table 4 Correlation coefficients among various heavy metals for six different sampling sites for Periyar River, Tamil Nadu, South India, during the study period from January 2012 to June 2013.

Heavy metals	B	Al	Cr	Mn	Fe	Ni	Cu	Se	Cd	Ba	Pb	Zn
B	1											
Al	-0.33258	1										
Cr	0.164293	0.189129	1									
Mn	-0.05549	0.499729	0.053713	1								
Fe	-0.35622	**0.558549**	0.194734	0.303891	1							

Ni	0.225758	0.321516	0.364489	0.280848	0.058827	1						
Cu	0.030465	-0.06586	-0.09959	0.067017	0.230693	-0.0552	1					
Se	0.266737	-0.07004	0.104004	-0.04667	0.057047	0.156301	0.218611	1				
Cd	0.315568	-0.22729	0.149549	-0.04206	-0.20365	0.442825	0.098296	0.270503	1			
Ba	**0.609368**	-0.16629	0.004136	-0.04156	-0.28012	0.01841	0.107266	0.336216	0.215222	1		
Pb	**0.509725**	-0.18237	0.028063	0.029393	-0.17588	0.286429	0.148471	0.213522	0.284193	**0.526492**	1	
Zn	0.326177	0.047762	0.14694	0.251002	0.064588	0.395567	0.334193	0.140334	0.185855	0.306169	**0.689764**	1

Table 5 Regression Equations for some pairs of heavy metals which have significant value of correlation

S.No	Parameters	R Value	Regression Equation	Statistical inference (P value < 0.01)
1	Pb & Zn	0.4758	Y=1.106 X – 26.212	Significant
2	Ba & B	0.3713	Y=0.156 X + 18.575	Significant
3	Fe & Al	0.312	Y= 0.1583 X + 62.663	Significant
4	Pb & B	0.2598	Y= 0.3249 X – 3.6706	Significant
5	Pb & Ba	0.2772	Y= 13.119 X – 72.363	Significant

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