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Comparative Study of Heavy Metal Contamination in Sediments of Yamuna river, Agra

Dr. Susan Jaison * Nisha Sidhardhan, Neeru Saxena and Anjali Mishra

*Department of Chemistry, St. John's College, Agra, **INDIA**

Email: susan.jaison@yahoo.com

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ABSTRACT

The comparative account of contamination levels of different heavy metals in sediments of Yamuna at Agra are compared with other river basin from worldwide and India. The concentration of heavy metal (Cr, Cu, Ni, Pb, Zn & Cd) are higher in the present study than the other sites, but Mn, Co, Fe is comparable to others. But comparison with lowest effect level (LEL) and probable effect level (PEL) shows that concentrations of all the metals are above these values and they may create any epidemic to aquatic biota and environment. Results of correlation matrix clearly indicate a moderate correlation between Cr/Pb, Fe/Cr, Cd/Cr, Cr/Cu, Cr/Zn and Cr/Ni, Pb/Mn, Mn/Fe, Mn/Ni, Pb/Zn, Pb/Ni, Cu/Fe, Fe/Ni, Zn/Cu, Zn/Ni and very strong correlation between Cu/Mn, Fe/Pb and a strong correlation was noticed between Zn/Mn, Pb/Cu. This correlation clearly indicates their possible common sources from heavy minerals or from urban centers as well as their common sink in stream sediments. Environmental risk assessment for metals was also calculated by evaluating anthropogenic factor, metal enrichment factor, pollution load index (PLI), sediment pollution index (SPI), geo-accumulation index (GAI).High metal enrichment factor was identified for cadmium. The EFm of metals in sediments were found in the order Cd>Pb>Cu>Zn>Cr>Ni>Co>Fe>Mn. High Efm values indicate the degrading quality of sediment. GAI (Geo Accumulation Index) was observed in the order Cd>Pb>Cu>Zn>Cr, while Mn, Fe, Co, Ni were found in class 0 indicate their background level. AG-9which is an agricultural site was found moderately polluted site according to sediment pollution index. But all the other sites were found highly to dangerously polluted. Hence, GAI and SPI clearly illustrate that sediment of Agra is moderately to dangerously polluted with these metals. Anthropogenic factors were calculated for each metal. It is estimated that 67% Cr, 80% Cu, 85% Zn, 79% Pb and 95% Cd were derived from anthropogenic input in the total heavy metal concentration. These values clearly explain that metals could easily enter to the bio cycle and could threat the lives of consumers at each level.

Keywords: Metal Enrichment Factor (EFm), Anthropogenic Fraction, Sediment Pollution Index (SPI),Pollution Load Index (PLI), Geo Accumulation Index (GAI).

INTRODUCTION

All the metals essential to life are toxic when present in excess of the optimum levels. Sediments are good indicators of the input of metal into receiving water, because settling biogenic and other particles act as a transporting carrier for heavy metal cations . The organic pollutants, mineral particles , the metal oxides and hydroxides help in removing the dissolved contaminants from water but increase the metal concentration in the sediment. Further dissolved matter is usually transported away from the outfall, while suspended wastes may be deposited in their point of origin and cause heavier concentration of these substances in sediments. There are no uniform distribution or incremental increase while going from sampling sites AG1-AG12. This is due to the variation in the human activity and the effluent discharge into the river. The result reveals that the sediment of river becomes rich in toxic metals. Humic colloids carrying elements becomes coagulated and get deposited in the sediment.

MATERIALS AND METHODS

After the initial survey of Yamuna river 12 sampling sites, AG1-AG12 (Fig.1) were chosen which cover entire river in Agra. Composite samples were collected from surface layer of sediments in three seasons over the period of two years **.**For analysis of trace metals, 5 g of each soil samples was weighed and transferred to 100 ml beaker for digestion. 20 ml of aqua regia (1:3, HNO3: HCl) was added to each soil samples and digested on a hot plate. Samples were slowly boiled and evaporated to about 10 to 15 ml. Before drying, again similar amount of aqua was added and covered with a watch glass and heated to obtain a gentle refluxing action. Continued heating and adding concentrated aqua regia was done until digestion was completed as shown by a light colored and clear solution. Digested samples was made up to 100 ml with water and filtered with a Whatman filter paper (No.1). Filtered samples were stored and analyzed for trace metals; Cd, Cr, Cu, Fe, Mn, Co, Ni, Pb and Zn by Atomic Absorption Spectrometer (AA Analyst 100, Perkin Elmer). All standards used were of A.R Grade.

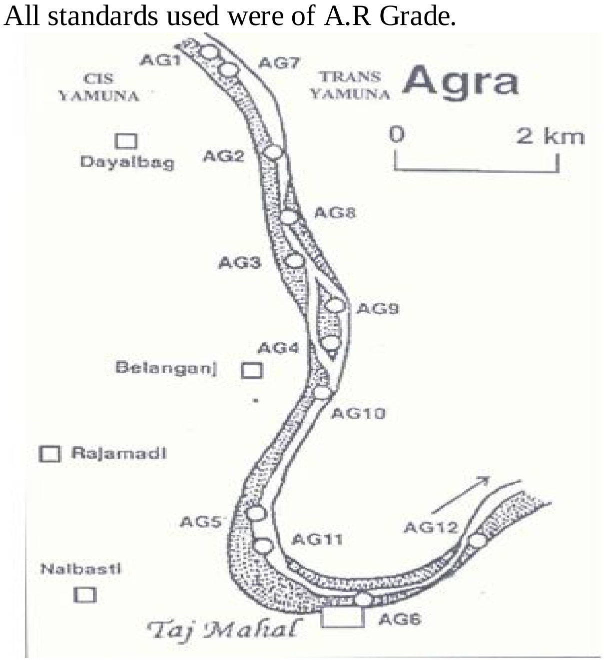

Fig. 1- Sampling sites AG1-AG12

RESULTS AND DISCUSSION

The metal concentrations present in sediments are determined by AAS with explanation discussed here.

Chromium: The overall average concentration of chromium was 280 mg kg^{-1} in the sediment of river Yamuna at Agra region. Cr is generally associated to be wear and tear produced products of automobiles body parts. The higher concentration of Cr was detected in the down streams of cis Yamuna (376 mg kg^{-1})

and trans Yamuna (317 mg kg^{-1}). Chromium toxicity result in irritation of gastrointestinal mucosa, Bronchopneumonia, Chronic bronchitis and trachietis .

Manganese: Mn is a vital micronutrient for both plant and animals, but excessive intake can cause manganisim and other problems related to stomach. Mn was ranged 384-775 mg kg^{-1} in the sediment.

Iron: Iron is directly associated with a high content of organic matter. The overall average concentration of Fe in the sediment of river Yamuna at Agra region was 39,088 mg kg^{-1}. Fe concentration was found of the highest at Trans Yamuna (downstream) with an average of 42754 mg kg^{-1}, followed by cis Yamuna (downstream) 3919±4161 mg kg^{-1}. The average Concentration of Fe in sediments of upstream were 34885 mg kg^{-1} (Cis Yamuna) and 38504 mg kg^{-1} (Trans Yamuna).
The highest Concentration of Mn and Fe in sediments are due to the effluent discharge by the number of Fe Foundries situated in Agra. As the sediment of river Yamuna is highly alkaline, these metals are precipitated as hydroxide under alkaline pH.

Lead: Lead is derived almost exclusively from the combustion of gasoline containing Pb and the knock additives. Concentration of Pb ranged from 31-266.8 mg kg^{-1} in the sediment of river Yamuna at Agra. The Pb deposition is not uniform, which reflux differences in the quantity of exhaust fumes deposition into the drains. The highest concentration of Pb was detected in the trans Yamuna 247 and 306 mg kg^{-1} river sediment than the cis Yamuna 38 and 175 mg kg^{-1} (table 1). Higher values for Pb in river sediment may be due to the atmospheric inputs from the vehicular emissions, prevalent usage of Pb pipes and discharges from industries situated in the adjacent areas. Durum et.al., shown that the solubility of Pb is low in alkaline surface waters and due to the rainfall and dust fall, Pb will be transferred to river sediment, where it tends to accumulate. Pb accumulates in myolin bone of animals and man, from where it can be excreted slowly. A large affinity of Pb^{2+} ions form thiols and phosphate containing ligands inhibit the biosynthesis of heme and there by effect the permeability of kidney, liver and brain cells.

Cadmium: The average concentration of Cd in the sediment of Agra river was 2-40 mg kg^{-1}. It was found maximum at AG6 40 mg kg^{-1} (table 1). This higher concentration of Cd was found in downstream of cis Yamuna 22 mg kg^{-1} and trans Yamuna 22 mg kg^{-1} compared to upstream cis Yamuna4 mg kg^{-1} and trans Yamuna 5 mg kg^{-1} . Cd is a toxic element for human as well as for environment. Drinking water containing excessive Cd led to the occurrence of itai-itai disease among the Japanese.

Copper: Cu is one of the essential components of numerous metalloenzymes and plays a vital role in the homopoieis, maintenance of vascular and skeleton integrity and function of nervous system. But the higher concentration of Cu causes toxicity of human beings include congestion of nasal mucous membranes and pharynx, stuffiness of the head. It may also cause edema of the eyelid.
The average concentrations of Cu in different sites of sediments were 401 mg kg^{-1}. The higher concentration of copper may be attributed to the heavy waste water discharge from industries.

Zinc: Among the micronutrients, Zn has been reported to be a limiting nutrient for normal yield. Excess of zinc affects the metabolism of humans by changing their minerals and enzyme budget especially in children and persons already suffering from a irregular metabolism. The concentration of zinc varied 496 at cis Yamuna (upstream) to 922 trans Yamuna (downstream)) in different sediments samples. The concentration of zinc is in trans Yamuna higher than cis Yamuna shows higher anthropogenic activities in trans Yamuna. Zn in sediment is the result of refused burning. Zinc toxicity causes muscular incardination, dizziness, renal failure and anemia.

Cobalt: Cobalt cannot be destroyed once it has entered the environment. It may react with other particles or adsorb on soil particles or water sediments. Cobalt will only mobilize under acidic conditions, but ultimately most cobalt will end up in soils and sediments. The overall average concentration of Co was found 18 mg kg^{-1}. Soils/sediments that contain very low amounts of cobalt may grow plants that have a deficiency of cobalt. But in excess it can cause polycythemia and respiratory ailments, cardiomyopathy, thyroid abnormalities.

Nickel: The concentration of nickel was found to be 112 mg kg^{-1} in different sites of sediment of river Yamuna at Agra region. It is almost similar in cis Yamuna upstream 96 mg kg^{-1} and downstream 97 mg kg^{-1} In trans Yamuna upstream 123 mg kg^{-1} and downstream 136 mg kg^{-1}. Nickel is mainly introduced in environment by detergents, smoking and it was found in many foodstuffs like chocolates. Nickel fumes are respiratory irritants and may cause pneumonitis.

Environment Rich Assessment: There are many methods for the environmental assessment on heavy metal pollution of sediment. When certain method is applied to assess the pollution extend of heavy metals, the factors including pollution caused by human geo-chemical background value and the formation and rotten effects of rock in nature that may change the background value of one metal element should be considered roundly [6].

Metal Enrichment Factor (**EFm**): One of the major problems in quantification of heavy metals enrichment in sediments is to know the base line concentration of heavy metals in unpolluted natural sediments. Generally average shale concentration given by Turekian and Wedepohl [3] is used as a worldwide standard to use it as a reference for unpolluted sediment. Metal enrichment factor was calculated by comparing average shale concentration .The EFm (table.1) progressively increases from the baseline to its highest level within a 15km long river at Agra. Such a high EFm can only be explained by the massive discharge of heavy metals rich urban effluents, draining directly in to rivers of the Yamuna. Cd is the highly enriched metal in the sediment of river Yamuna. The order of enriched metals in sediment are Cd>Pb>Cu>Zn>Cr>Ni>Co>Mn (fig 2). These toxic metals get precipitated along with surface sediment and causes degradation of sediment quality. Similar results have been found by the Singh et.al, [5] for Yamuna river, Agra and explained that these sediments are adversely affecting the ecological functioning of rivers due to heavy metals mobilizations from urban sphere into biosphere. For Socio-economic growth urban development plans should be regional than localized in nature to keep its freshwater rivers free from sediment pollution for the future [3].

Anthropogenic Fraction: Considering average shale concentration as lithogenic fraction, source of anthropogenic fraction in total heavy metal concentration of stream sediment was also estimated. High percentage of anthropogenic fraction indicates tremendous easy availability of these toxic metals to biotic components of rivers ecosystem of the Yamuna. It may enter into the food chain and may impact millions of people in one or another way. In surface sediments the concentration of heavy metals from anthropogenic sources were as high as 70% of Cr, Cu, Zn, Pb and Cd. Overall average of 67% Cr, 80%Cu, 85%Zn, 79%Pb and 95%Cd of total heavy metal concentration were derived from anthropogenic sources. (fig.2). Such behavior of heavy metal distribution in sediments were also seen in the lower Rhine river (Germany) and by Singh in Ganga plan, where more than 90% of Cu, Pb, Zn and more than 99% of Cd were originated from anthropogenic source. High percentage of anthropogenic fraction indicates tremendous easy availability of these toxic metals to biotic components of rivers ecosystem. It may possibly enter into the food chain under suitable physico-chemical conditions and exposing millions of people in one or another way[4].

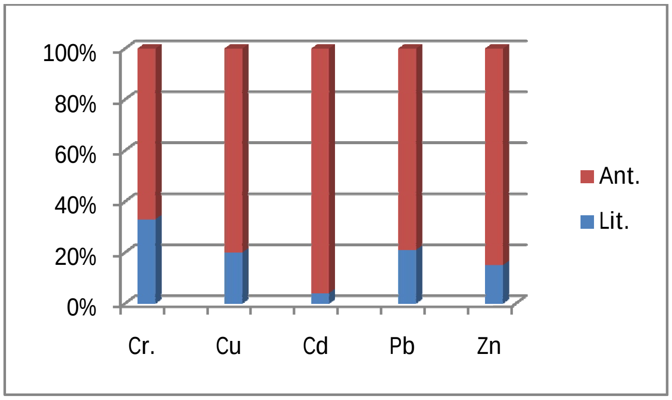

Fig.2.Anthropogenic and Lithogenic Fraction

Sediment Pollution Index (SPI): It may be defined as a linear sum of the metal enrichment factors along with the account of metal toxicity weight which is based on the relative toxicity of different metals and are inversely proportional to lithogenic limits of average shale. It is assigned 1 for Cr and Zn as less toxic elements, 2 for Ni and Co, 5 for Pb and 300 for Cd. It is calculated as

$$SPI= \frac{\Sigma(EFm*Wm)}{\Sigma Wm}$$

Where, EFm= Ratio between sediment total content in a given sample and average shale concentration of a metal m.

Wm= Toxicity weight of metal m.

Surface sediments from Agra are categorized into moderately polluted to dangerous sediments as its SP1 class ranges from SP12-SP14 (Table.1).It can be easily noticed from graph that AG6 has maximum sediment pollution index. [5]

Table. 1- Sediment pollution index (SPI) of Yamuna river sediment

Sampling Sites	**Sediment Pollution Index**	**Sediment Quality**
AG1	13.63	Highly polluted
AG2	13.91	Highly polluted
AG3	17.13	Highly polluted
AG4	42.49	Dangerous
AG5	48.96	Dangerous
AG6	129.14	Dangerous
AG7	7.11	Moderately polluted
AG8	24.31	Dangerous
AG9	20.18	Dangerous
AG10	50.66	Dangerous
AG11	76.23	Dangerous
AG12	95.34	Dangerous

Pollution Load Index (PLI): PLI is used in order to find out the mutual effects of the different studied metals. It is calculated according to the equation given by Tomilson et.al and Frostner. It is also used to understand the Impact of urbanization activities on sediment quality.

$$PLI = \sqrt[n]{EF\ of\ Cd * EF\ of\ Pb * EF\ of\ Cu * EF\ of\ Zn * EF\ of\ Ni * EF\ of\ Cr}$$

Where, EF is the enrichment factor. In the present case, n which stands for Cr, Ni, Cu, Zn, Pb and Cd is 6. The PLI values for surface sediments of Yamuna at Agra were found to be 1.7, 2.3, 2.4, 3.0, 3.1, 2.7, 2.8, 3.0, 3.1, 3.5 and 3.3 for sampling sites AG_1, AG_2, AG_3, AG_4, AG_5, AG_6, AG_7, AG_8, AG_9, AG_{10}, AG_{11} and AG_{12} respectively. These high PLI values (Fig.3) show direct linear relationship with industrial processes and urbanization. The present study is critical and could be used as reference in establishing appropriate urban planning of the Agra.

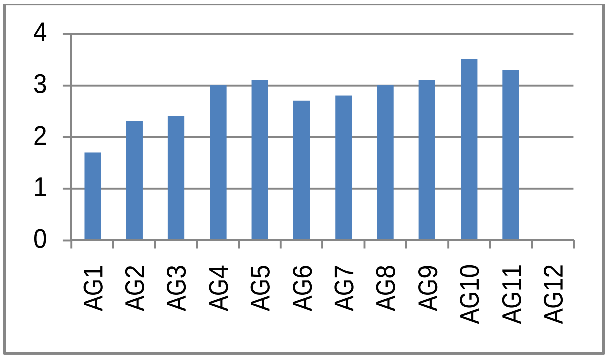

Fig.3. Pollution load index

Geo Accumulation Index (GAI): It is a quantitative measures to assess the contamination of heavy metal in sediment from the view of environ-geography chemistry. It was proposed by Miller and can be calculated by following formula given below.

$$I_{geo=}\ Log_2\ [\ C_n/1.5*B_n]$$

Where C_n= Measured concentration of heavy metal in number of the sediment.

B_n= Shale concentration or Geo-Chemical background data or shale concentration.

The factor 1.5 is used for possible variations in background data due to lithogenic effect. Based on the Index, Fe, Co, Ni, and Mn remain in class O' suggesting that these metals are in background values. Cu, Cr, and Zn; 1-3,1-2,1-3, a geo-accumulation rating of class 1 to class 3,where as Pb have rating of class1-4 classifying Agra sediment as moderately to dangerously polluted with these metals. Cd attains the class 2 to 6 indicating that surface sediments of the Agra are highly polluted with these metals. Fresh water sediment quality guiding provide another criteria for the evaluation of heavy metal concentration in river sediments in response to adverse effect on the rivers biological components.

Lowest Effect Level (LEL) and Probable Effect Level (PEL): Comparative study of heavy metal concentration of lowest effect level (LEL) and probable effect level (PEL). In the LEL sediments are considered to be clean but marginally polluted, but no effects on the majority of sediment-dwelling organism are expected below this concentration.[1]. The Probable effect level (PEL)represents the level above which adverse effect to aquatic biota are predicated to occur frequently using this approach in the Yamuna river sediment, all the metals were found above the LEL and PEL concentration. Hence, these metals may cause sediment toxicity to the fresh water ecosystem of Yamuna water.

Comparison to other studies: Heavy metal concentrations in the sediments of the Yamuna were compared to other river basin of India (table .2). It indicates that Yamuna river at Agra has higher values of metals than other literature values except Co, Fe and Mn, the concentration of other elements in Yamuna sediment is not comparable with respect to other studies. High concentration of metals indicates the degradation of sediment and water quality..

Table -2. Comparison study of heavy metal concentration (mg/kg) to sediments of the Yamuna river with other systems and the world.

Heavy metals	Ganges river sediments 1	Yamuna river Sediments 2	Ganges Delta Sediments 3	Bay of Bengal Sediments 4	Cauvery Sediments 5	Average Shale 6	Indian river Sediment Average 7	World Average 8	Present study
Cr	147	70	97	84	95	90	87	100	308
Mn	1765	460	1075	529	560	850	607	1050	643
Fe	40,350	25,000	48,000	39,800	29,950	46,000	29,000	48,000	39088
Co	19	-	-	-	25	19	-	20	18
Ni	47	20	28	64	55	68	37	90	112
Cu	55	40	25	26	26	45	28	100	401
Zn	105	70	76	-	92	95	16	350	771
Cd	0.58	-	-	-	2.1	0.30	-	-	15
Pb	22	-	17	-	20	20	-	-	195

APPLICATIONS

The information about the distribution of pollutants in sediment can be of value in assessing the potential impact of sediment suspension upon water quality as sediment is an ultimate sink and the characteristics of sediment reflect the current quality of the Yamuna water at Agra region.

CONCLUSIONS

Yamuna river at Agra has higher values of metals than other literature values except Co, Fe and Mn. It is therefore concluded that Urbanization process is destroying a natural process of self purification of river.

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