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Comparative Study of Heavy Metal Concentrations in Yamuna River Sediment and Other Rivers

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ABSTRACT

A comparison of total metal concentrations in the water and sediment with the shale standard is generally taken as a quick and practical method of tracing heavy metals enrichment. The average shale values along with the metal concentrations reported by other workers on some of the major rivers of the world. In most of the cases the average total heavy metal (Cr, Cu, Fe, Mn, Ni and Zn) concentrations determined in Yamuna river sediments was found to be lower than the corresponding shale values except Cd and Pb. The cadmium concentration in the Yamuna river sediments was found to be more than 6 times higher (1.83 µg/g) than that of shale (0.30 µg/g), while lead concentration was 1.5 times higher (30.47 µg/g) than that of shale (20.0 µg/g). Overall the heavy metal concentration in the Yamuna river sediment is in good agreement with the shale standard. We have reported higher concentration of Cr, Cu, Fe, Mn, Ni and Zn in the bed sediment of the river Ganga, as compared to the results of present study whereas the Cd and Pb concentrations observed in the present study is higher than Ganga river sediments, also reported higher concentrations of Cd, Cr, Cu, Fe, Mn, Ni and Zn in Cauvery river system. When we compared our result with the Neckar River, the concentrations of metals in the bed sediment of river Yamuna were found lower than those of the Neckar river except Cd. Lead and Zn concentrations were found high in our study than Ganga river. Lead concentration in Yamuna river sediments was found higher than Guadairriver. A comparison of the present study result with the other rivers reveals that the average concentration of Cd and Pb are high in the Yamuna river sediments.

Keywords: Temperature, Water, water pollution, Yamuna River, sediment

ARTICLE INFO

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1. Introduction

India has a large number of rivers that are lifelines for the millions living along their banks. These rivers can be categorized into four groups: Rivers that flow down from the Himalayas and are supplied by melting snow and glaciers. This is why these are perennial, that is, they never dry up throughout the year. The Deccan Plateau rivers, which depend on rainfall for their water the coastal rivers, especially those on west coast, which are short and do not retain water throughout the year the rivers in the inland drainage basin of west Rajasthan, which depend on the rains. These rivers normally drain towards silt lakes or flow into the sand. Rivers are the most important freshwater resource for human. Social, economic and political developments which, in the past, have been largely related to the availability and distribution of fresh water contained in riverine systems. Major river water uses can be summarized as follows: (Chapman, 1992).

- Ñ potable water supply,
- Ñ irrigation of agricultural lands,
- Ñ industrial and municipal waste disposal,
- Ñ navigation,
- Ñ fishing and body-contact recreation,
- Ñ Aesthetic value.

The classification of rivers according to their discharge is generally more satisfactory, but has not, to date, been completely defined and accepted. However, there are certain specified discharge rates, which are widely used to characterize river discharges and their annual variations. These include the average peak discharges, the monthly or annual average discharge and the average low discharge. A size classification based on discharge, drainage area and river width is given in Table 1.

There are thirteen major river basins (area more than 20,000 km²) in the country, which occupy 82.4 % of total drainage basins, contribute 85 % of total surface flow and house 80 % of the country's population. Major river basins are Brahmaputra, Ganga (including Yamuna Sub Basin), Indus (including Satluj and Beas Sub Basin), Godavari, Krishna, Mahanadi, Narmada, Kauvery, Brahmini (including Baitarni Sub Basin), Tapi, Mahi, Pennar and Sabarmati. The classification of river basin based on catchment area is given in Table 2.

River water and sediment

Most chemical reactions involving dissolution of solids are accelerated by increased temperatures. The solubility of gases, on the other hand, decreases at elevated temperatures. Because biological oxidation of organics in streams and impoundments is dependent on an adequate supply of dissolved oxygen, decrease in oxygen solubility is undesirable. Temperature also affects other physical properties of water. The temperature of surface water is influenced by factors such as latitude, elevation, season, time of day, rate of flow and depth. During the study period, temperature was recorded ranged between 18.75 -

29.67 °C. The different temperature at different locations during the same seasons was due to the different sampling time on the same day. The hydrogen (H⁺) and hydroxyl (OH⁻) ions are controlling variables in aqueous systems as they influence both physico-chemical and biological processes in the aquatic environment. The equilibrium between these two ionic species is influenced by reaction with acids and bases introduced into the aqueous system. pH, an indicator of acidity is a measure of water's ability to neutralize base. The sediment of river Yamuna is characterized with alkaline pH throughout the study period and ranged between 7.30 and 8.24. The organic matter content varied between 0.35 and 14.26 %. A higher percentage of silt in the sediment results in a very loose fabric with a very high porosity and high permeability, resulting in easy transportation of the sediment downstream (Singh et al., 2005).

Heavy metals in Yamuna River

Many heavy metals of toxicological significance have low solubilities in the range of Eh and pH conditions found in natural waters and river sediments act as sinks for trace metals mobilized in the drainage basin (Salomons and Forstner, 1984). Bed sediment metal contents reflect the influence of catchment lithology, anthropogenic contamination and chemical reactions (precipitation, complexation, and adsorption) between the water column and the sediment particle surfaces. Transport, deposition, resuspension and solubilization of these metals in the fluvial system is dominated by hydrological processes and by the chemistry of the water column (Foster and Charlesworth, 1996).

Heavy metals in river sediments

The concentrations of heavy metals in sediments were found considerably higher than those observed in river water. The concentration of the heavy metals in Yamuna river sediments ranged as, Cd (ND -12.74); Cr (0.26 - 40.16); Cu (ND - 158.40); Fe (1724.20 - 15788.10); Mn (37.18 - 641.40); Ni (1.04 - 62.04); Pb (ND - 125.70); and Zn (ND - 273.60) mg/g, respectively. It may be noted that in bed sediments the mean concentrations of all the metals, except Cu, were relatively higher at site S-4, while Cu was found higher at site S-7. The river receives high inputs of mixed domestic and industrial wastewater (about 450 MLD) between site S-3 and S-4. Moreover, a barrage constructed upstream of site S-5 restricts the river flow and causes settling of suspended matter along with adsorbed metals in this stretch

2. Materials and Methods

Study area

The Yamuna River, one of the major tributaries of the Ganga river system in northern India has been selected for this study. It has been acclaimed as a holy river in Indian mythology and various pilgrimage centers e.g. Yamunotri (Uttaranchal), Paonta Sahib (Himachal Pradesh), Mathura, Vrindavan, Bateshwar & Allahabad (all in Uttar Pradesh)

are located at the banks of this river. Large urban centers e.g. Yamuna Nagar, Sonapat, Delhi, the political nucleus of India, Gautam Budh Nagar, Faridabad, Mathura, Agra and Etawah are also established on its banks. The total length of Yamuna River from origin at Saptrishi Kund to its confluence with Ganga at Allahabad is 1376 km traversing through five states. The main stream of river originates from the Yamunotri glacier (Saptrishi Kund) near Bander punch peaks ($38^{\circ} 59' N 78^{\circ} 27' E$) in the Mussoorie range of the lower Himalayas at an elevation of about 6320 meter above mean sea level in Uttarkashi district of Uttaranchal.

In the present study, total ten sites (Figure 3.1), namely Bagpat (Site-1), Sonipat (Site-2), Pallo (Site-3), Nizamuddin bridge (Site-4), Palwal (Site-5), Agra canal (Site-6), Agra upstream (Site-7), Agra downstream (Site-8), Bateshwar (Site-9) and etowh (Site-10) were selected to assess the impact of localized domestic and industrial effluents and the heavy metal concentrations and their speciation forms in sediments of the Yamuna river. The first two sites (1-3) are located in the area of relatively low river pollution. Other four sites (3-6) are located in the region of high river pollution as there are a number of wastewater drains and two highly polluted tributaries emptying into the river in this stretch. The last four sites (7-10) are in the downstream region of moderate pollution as the river considerably recovers in the course. The river water during the study period are presented in the Table 3. The river water temperature during the study period ranged between 18.75 - $29.67^{\circ}C$. The minimum temperature was observed during the winter at site S-6 ($18.75^{\circ}C$), and maximum during the summer at site S-2 ($29.67^{\circ}C$). The river water pH was observed alkaline throughout the study period ranged between $8.08 - 8.62$. The minimum pH was observed at site S-5, and maximum at site S-10.

Sampling and analysis of river sediments

The bed sediments samples were collected from shallow water about 20 m from the bank at three points (1/4, 1/2, 3/4) across the river width at all the 10 sites during the study period ((March, 04; June, 04; Sept., 04; Dec., 2011; March, 05; June, 05; Sept., 05 and Dec., 2012), using grab sampler and kept in polythene bags. The samples were air dried for removal of water contents associated with the sediments. The dried samples were then ground with pestle mortar, homogenized, sieved to below 100 mesh size, sealed in clean polythene bags and stored in refrigerator for characterization and speciation (Sakai et al., 1986).

pH measurement in 1:2 sediment water suspension

The pH value is a measure of the hydrogen ion activity of the soil/sediments water system and expresses the acidity and alkalinity of soil/sediments. The pH of a solution has been defined as the negative logarithm of the hydrogen ion activity, which in very dilute solutions can be expressed as concentration, in gram mole per litre.

$$pH = -\log_{10}[H^{+}] \text{ or } [H^{+}] = 10^{-pH}$$

Procedure

Prepare 1:2 sediments water suspension, weighed 40.0 g dry sediment sample into 250 ml conical flask and add 80 ml of double distilled water, stopper the flask and shake the mixture on the reciprocating shaker for one hour. Allowed

the suspension to settle for 30 minutes. Measure the pH in unfiltered suspension using a glass electrode (Khawaja et al., 2000, Singh et al., 2005) pH meter (Metrohm, Model No. 740).

Particle size analysis

Bouyoucos Hydrometer method (Kalra and Maynard, 1991): The mineral part of the soil is separated into different-size fractions. The proportions of these fractions are determined by the sedimentation principle based on Stokes' law, which relates the radius of the particles to the velocity of sedimentation. The following particles are determined by the hydrometer method:

diameter	Sand	0.05	to	2.0	mm
diameter	Silt	0.002	to	0.05	mm
	Clay	< 0.002 mm diameter			

Equipment and reagents

- American Standard Testing Methods soil hydrometer, 152H ($20^{\circ}C$) with bouyoucos scale (0 - 60 g/l).
- Electric stirrer.
- Metal dispersing cups.
- Glass sedimentation cylinders measuring to 1 litre and 1.130 litre.
- Stop watch.
- Thermometer range (10 - $50^{\circ}C$).
- Sodium hexa-metaphosphate solutions, containing 50.0 g salt per litre of distilled water.

Method

1. Weigh 50.0 g oven dry sediment which was ground and sieved through 2 mm opening sieve. Soak overnight in a beaker containing 50 ml of sodium hexa-metaphosphate solution and 100 ml of double distilled water.
2. Disperse the sample in suspension by transferring it from the beaker to a one litre mixing cup and stirred with an electric stirrer for 5 min.
3. Transfer the mixed suspension to a glass sedimentation cylinder. Make volume to the mark (1.130 liter) by adding distilled water, while density hydrometer in the suspension.
4. Remove the density hydrometer from the suspension. Stopper the opening of the cylinder with a rubber cork bang. Mix the sediment suspension by turning the cylinder upside-down ten times. Placed on level surface in a room with constant temperature. Start a stop watch immediately and take reading of the hydrometer at 40 second and 2 h. always immerse the hydrometer slowly in the suspension, approximately 10 second before each reading, and remove it immediately but slowly following each reading.
5. Measure the density of the blank solution of sodium hexa-meta phosphate, made up to the 1.130 litre volume mark, in the cylinder.
6. Measure the temperature of the suspension and correct the hydrometer reading by 0.2 for each degree Fahrenheit above the temperature of $67^{\circ}F$ (the

hydrometer type ASTM no. 152H was calibrated at 67^oF).

Calculation

For every 1°C above or below 20°C, 0.36 graduations of the hydrometer are added to or subtracted from the reading. The correct hydrometer readings are obtained by correcting for temperature and subtracting the blank reading.

$$(a) \text{ Silt + Clay (\%)} = \frac{\text{Corrected hydrometer reading at 40 seconds}}{\text{Sample weight (g)}} \times 100$$

$$(b) \text{ Clay (\%)} = \frac{\text{Corrected hydrometer reading at 2 h}}{\text{Sample weight (g)}} \times 100$$

$$(c) \text{ Silt (\%)} = (a) - (b)$$

$$(d) \text{ Sand (\%)} = 100 - (a)$$

3. Results and Discussion

The metal concentrations (total) in the sediment with the shale standard is generally taken as a quick and practical method of tracing heavy metals enrichment. The cadmium concentration in the Yamuna river sediments was found to be more than 6 times higher (1.83 µg/g) than that of shale (0.30 µg/g), while lead concentration was 1.5 times higher (30.47 µg/g) than that of shale (20.0 µg/g). Overall the heavy metal concentration in the Yamuna river sediment is in good agreement with the shale standard. Singh et al. (2003) have reported higher concentration of Cr, Cu, Fe, Mn, Ni and Zn in the bed sediment of the river Ganga, as compared to the results of present study whereas the Cd and Pb concentrations observed in the present study is higher than Ganga river sediments. Vaithiynathan et al. (1993) have reported higher concentrations of Cd, Cr, Cu, Fe, Mn, Ni and Zn in Cauvery river system. When we compared our result with the Neckar river, the concentrations of metals in the bed sediment of river Yamuna were found lower than those of the Neckar river (Muller et al., 1993) except Cd. Lead and Zn concentrations were found high in our study than Ganga river (Saika, 1987). Lead concentration in Yamuna river sediments was found higher than Guadairariver (Gonzalez et al., 2000). A comparison of the present study result with the other rivers reveals that the average concentration of Cd and Pb are high in the Yamuna river sediments.

Correlation matrix of heavy metals in river water

Correlation analysis was performed on heavy metals at each site to assess possible co-contamination from similar sources. The correlation matrix of heavy metals in Yamuna river water exhibits significant positive correlation ($p < 0.05$) values between Cu-Ni ($r = 0.131$), Fe-Ni ($r = 0.137$), Mn-Ni ($r = 0.162$), and Ni-Pb ($r = 0.138$), and there was also highly significant positive correlation ($p < 0.01$) was found between Cr-Ni ($r = 0.421$), Cr-Pb ($r = 0.167$), Cu-Zn ($r = 0.178$), Fe-Mn ($r = 0.561$), Fe-Zn ($r = 0.510$), Mn-Zn ($r = 0.532$), and Ni-Zn ($r = 0.194$). No significant correlation was observed between Cd and other metals, this may be due to their different origin than other metals.

Correlation matrix of heavy metals in river sediments

The correlation matrix of heavy metals in Yamuna river sediments exhibits positive correlation ($p < 0.01$) between Cd-Cr ($r = 0.519$), Cd-Cu (0.347), Cd-Fe (0.306), Cd-Mn (0.550), Cd-Ni (0.682), Cd-Pb (0.685), Cd-Zn (0.577), Cr-Cu (0.424), Cr-Fe (0.519), Cr-Mn (0.641), Cr-Ni (0.645), Cr-Pb (0.525), Cr-Zn (0.531), Cu-Fe (0.227), Cu-Mn (0.327), Cu-Ni (0.307), Cu-Pb (0.283), Cu-Zn (0.446), Fe-Mn (0.586), Fe-Ni (0.709), Fe-Pb (0.554), Mn-Ni (0.784), Mn-Pb (0.773), Mn-Zn (0.473), Ni-Pb (0.871), Ni-Zn (0.429), and Pb-Zn (0.413). No significant correlation was observed between Fe and Zn.

In natural river systems, elements as well as metals exist together in relative proportion to each other. These ratios depend on a large number of processes in a geochemical cycle including weathering, transport and deposition (Jain, 2004). Iron normalized heavy metal concentrations (M/Fe) in Yamuna river sediments from Neemsar to Jaunpur D/S are presented in the Table 6. The metal pair ratio clearly reflects maximum enrichment of all studied metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) at site S-4 followed by site S-5 for Cd, Cr, Cu and Zn, and site S-6 for Mn, Ni and Pb. The spatial trends of metal enrichment in bed sediments of the Yamuna river are in agreement with the data reflecting sources/activities of the corresponding catchments regions. Jain (2004) studied the metal enrichment in Yamuna river sediment and found the maximum enrichment of Cu followed by Pb and Cd at site where anthropogenic activities are high.

Speciation/fractionation of heavy metals in Yamuna river sediments

In the present study, sequential extraction procedure as proposed by Tessier et al. (1979), has been used to obtain the following five geo-chemical fractions: (1) exchangeable fraction; (2) carbonate fraction; (3) Fe-Mn oxide fraction; (4) organic fraction; and (5) residual fraction. The speciation patterns of different heavy metals viz., Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the Yamuna river sediments at 10 different sites.

Cadmium (Cd)

The fractionation profile of Cd in Yamuna river sediments in summer 04, Cd was mostly bound with residual fraction (78.13 %) at site S-9 followed by carbonate fraction (56.79 %) at site S-1, exchangeable fraction (47.80 %) at site S-4, Fe-Mn oxide fraction (29.63 %) at site S-1 and organic fraction (13.58 %) at site S-1. While in winter 05, a major fraction of Cd was bound with residual fraction (100 %) at site S-1.

Chromium (Cr)

The fractionation profile of Cr in summer 04 indicates its dominant presence with the residual fraction (98.07 %) at site S-10 followed by carbonate fraction (33.79 %) at site S-9, and organic fraction (25.37 %) at site S-5. However, in winter 05 the Cr was mostly associated with the residual fraction of the sediment (90.54 %) at site S-9, whereas, a smaller fraction was also bound with the organic fraction (15.12 %) at site S-1.

Copper (Cu): The fractionation profile of Cu in summer 04 shows that its major portion was associated with the organic

fraction (59.57 %) at site S-4 followed by residual fraction (43.71 %) at site S-10 and carbonate fraction (22.86 %) at site S-1. A smaller portion was also associated with the Fe-Mn oxide fraction (4.64 %) at site S-1 and exchangeable fraction (3.47 %) at site S-6.

Iron (Fe)

The fractionation profile of Fe in Yamuna river sediments in the summer Fe was mostly bound with residual fraction (86.54 %) at site S-9 followed by organic fraction (19.33 %) at site S-1, whereas, a smaller portion was also associated with the carbonate fraction (6.30 %) at site S-1, Fe-Mn oxide fraction (4.74 %) at site S-1 and exchangeable fraction (0.31 %) at site S-10. The fractionation profile of iron in winter 05, shows that its major portion is associated with the residual fraction (91.55 %) at site S-4.

Manganese (Mn): The fractionation profile of Mn shows that its major portion is associated with the residual fraction (58.29 %) at site S-9 followed by carbonate fraction (22.38 %) at site S-3, exchangeable fraction (21.07 %) at site S-10, and organic fraction (16.80 %) at site S-8 in summer 04. While in winter 05, a major portion of Mn was bound with the residual fraction (63.61 %) at site S-5.

Nickel (Ni)

The fractionation profile of Ni in summer 04 indicates its affinity towards residual fraction (83.40 %) at site S-10 followed by carbonate fraction (38.17 %) at site S-1 and organic fraction (17.29 %) at site S-4, whereas, a smaller portion was also bound with Fe-Mn oxide fraction (8.71 %) at site S-7 and exchangeable fraction (3.45 %) at site S-5. However, in winter 05, Ni was observed mostly associated with the residual fraction (76.55 %) at site S-10 of the sediment followed by exchangeable fraction (33.06 %) at site S-8, carbonate fraction (11.96 %) at site S-3.

Lead (Pb)

The fractionation profile of Pb in Yamuna river sediments in summer 04, the fractionation profile of Pb shows that its major portion is associated with the residual fraction (63.54 %) at site S-9 followed by carbonate fraction (51.81 %) at site S-1, and in organic fraction (26.18 %) at site S-10. A smaller portion was also bound with exchangeable fraction (12.59 %) at site S-9 and Fe-Mn oxide fraction (11.93 %) at site S-9.

Zinc (Zn): The fractionation profile of Zn shows that its major portion was associated with the residual fraction (75.03 %) at site S-10 followed by organic fraction (38.00 %) at site S-1, and exchangeable fraction (31.11 %) at site S-4. A small fraction of Zn was also found to be associated with the Fe-Mn oxide fraction (20.28 %) at site S-8 and carbonate fraction (14.41 %) at site S-5. However, in winter

05, the major portion of Zn was bound with the residual fraction (88.84 %) at site S-1 followed by exchangeable fraction (29.042 %) at site S-8.

Discussion

Fractionation/speciation of the heavy metals in Yamuna river sediments

Sediments conserve important environmental information (Gutierrez et al., 2004) and are increasingly recognized as both carriers and possible sources of contaminants in aquatic system (Tessier et al., 1979). An evaluation of total metal concentration levels after a strong acid digestion of the sediments may be useful for global budget calculation, but it provides little information on the potential availability of metals to biota under various environmental conditions. Since the mobility of trace metals, as well as their bioavailability and related ecotoxicity, critically depend upon the chemical forms in which metals are present in the sediments, considerable interest exists in trace element speciation (Davidson et al., 1994). It is widely reported that the partitioning of metals between phases, or metal speciation, is of critical importance to the potential toxicity and mobility of contaminant metals released into the fluvial environment through either natural or anthropogenic processes (Forstner et al., 1981; Calmano and Forstner, 1983; Macklin and Dowsett, 1989; Bradley, 1995; Baruah et al., 1996; Buykx et al., 2000). Given the importance of metal speciation, it has been widely argued that the nature of metal partitioning in the sedimentary environment may be of more importance than the total metal concentrations of heavy metals (Ma and Rao, 1997; Barona et al., 1999). Indeed, Mester et al.(1998) argued that determining the total content of heavy metals is insufficient to assess the potential environmental impact of contaminated sediments. This is because only a small proportion of the metal present may take part in short-term geochemical processes and/or be bio available (Forstner and Kersten, 1988).The method used in the present study was adapted from the Tessier scheme. Exchangeable fractions - Organic fractions represent 'labile' fractions since they are removed by extract ants, which do not destroy the native minerals of sediments. Exchangeable fraction is assumed to represent water-soluble constituents plus readily exchangeable ions. The Tessier method extracts 'specifically sorbed or carbonate bound' ions with sodium acetate buffered to pH 5.0. Zwarich and Mills (1971) recommended this extractant for the quantitative determination of sedimentary calcite and dolomite. Metals found in this phase are expected to be chemically stable and biologically inactive (Tessier et al., 1979).

Table 1. Classification of rivers based on discharge characteristics and the drainage area and river width

River size	Average discharge (m ³ /s)	Drainage area (km ²)	River width (m)	Stream order ¹
Very large river	> 10,000	> 10 ⁶	> 1,500	> 10
Large river	1,000 - 10,000	100,000 - 10 ⁶	800 - 1,500	7 - 11
Rivers	100 - 1,000	10,000 - 100,000	200 - 800	6 - 9
Small rivers	10 - 100	1,000 - 10,1000	40 - 200	4 - 7
Streams	1 - 10	100 - 1,000	8 - 40	3 - 6
Small streams	0.1 - 1.0	10 - 100	1 - 8	2 - 5
Brooks	< 0.1	< 10	< 1	1 - 3

Depending on local conditions, Source: Chapman (1992).

Table 2. Classification of River Basin in India

River Basin	Catchment Area – km ² (%)	No. of Basin
Major	> 20,000 (82.4)	13
Medium	2,000 - 20,000 (8)	48
Minor	< 2,000 (9.6)	52

Source: Bhardwaj (2005).

Table 3: Characteristics of sampling sites

Sites	District	Water temperature °C			pH
		Summer	Monsoon	Winter	
S-1	Bagpat	29.50	28.63	19.38	8.40
S-2	Sonipat	29.67	29.25	19.38	8.60
S-3	Palla	28.67	29.00	20.25	8.59
S-4	Nizamuddin bridge	29.33	29.00	20.50	8.33
S-5	Agra canal	28.33	28.75	20.13	8.08
S-6	Palwel	27.33	28.50	18.75	8.53
S-7	Agra upstream	29.00	29.63	19.75	8.54
S-8	Agra downstream	29.67	28.38	19.75	8.55
S-9	Bateshwar	28.67	27.63	19.38	8.60
S-10	Etawah	29.00	27.50	19.63	8.62

Mean values of temperature and pH, measured during study period.

Table 4. Correlation matrix of heavy metal concentrations in Yamuna river water, n=240

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1							
Cr	0.002	1						
Cu	0.005	0.098	1					
Fe	0.039	0.030	0.120	1				
Mn	0.001	-0.016	0.085	0.561**	1			
Ni	-0.011	0.421**	0.131*	0.137*	0.162*	1		
Pb	-0.014	0.167**	-0.029	-0.038	-0.044	0.138*	1	
Zn	0.026	-0.008	0.178**	0.510**	0.532**	0.194**	-0.035	1

*Correlation is significant at the level $p < 0.05$. **Correlation is significant at the level $p < 0.01$.

Table 5. Correlation matrix of heavy metal concentrations in Yamuna river sediments, n=234

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1							
Cr	0.519**	1						
Cu	0.347**	0.424**	1					
Fe	0.306**	0.519**	0.227**	1				
Mn	0.550**	0.641**	0.327**	0.586**	1			
Ni	0.682**	0.645**	0.307**	0.709**	0.784**	1		
Pb	0.685**	0.525**	0.283**	0.554**	0.773**	0.871**	1	
Zn	0.577**	0.531**	0.446**	0.125	0.473**	0.429**	0.413**	1

**Correlation is significant at the level $p < 0.01$.

Table 6: Correlation coefficients for the relationship between total metal concentrations in river sediments with pH and organic matter (OM), n=10

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
pH	-0.898**	-0.719	-0.861**	-0.536*	-0.658*	-0.696*	-0.714*	-0.807**
OM	0.972**	0.883**	0.949**	0.686*	0.762*	0.818**	0.839**	0.926**

* Correlation is significant at the level $p < 0.05$. **Correlation is significant at the level $p < 0.01$.

Table 8: Comparative study of heavy metals in Yamuna river sediments with other rivers of the world & average shale value

Rivers	Cd (Mg/g)	Cr (Mg/g)	Cu (Mg/g)	Fe (Mg/g)	Mn (Mg/g)	Ni (Mg/g)	Pb (Mg/g)	Zn (Mg/g)	Reference
Ganga	0.58	147.00	55.00	40,350	1765.00	47.00	22.00	105.00	Singh <i>etal.</i> (2003)

Ganga	2.55	-	10.80	-	-	-	25.60	36.10	Saika (1987)
Brahmaputra	-	-	17.00	-	-	-	-	47.00	Subramanian <i>et al.</i> (1987)
Yamuna	-	70.00	40.00	25,000	460.00	20.00	-	70.00	Jha <i>et al.</i> (1990)
Yamuna	9.5	-	22.20	-	-	-	60.30	59.20	Jain (2004)
Cauvery	2.10	95.00	26.00	29,950	560.00	55.00	20.00	92.00	Vaithiyanathan <i>et al.</i> (1993)
Guadaira	3.00	38.00	25.00	25,000	477.00	37.00	20.00	51.00	Gonzalez <i>et al.</i> (2000)
Neckar	1.81	13.00	108.00	23,700	496.00	44.00	74.00	370.00	Muller <i>et al.</i> (1993)
Gomti	2.42	8.15	5.00	26,609	148.13	15.17	40.33	41.67	Singh <i>et al.</i> (2005)
Yamuna	1.83	10.97	10.53	5,898	174.41	14.69	30.47	39.91	Present study
Average shale	0.30	90.00	45.00	46,700	850.00	68.00	20.00	95.00	Turekian & Wedepohl (1961)

Table 9: Correlation matrix of heavy metals in different fractions (Summer-04), n=10

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Exchangeable fraction								
Cd	1.000							
Cr	ND	ND						
Cu	0.773	ND	1.000					
Fe	-0.088	ND	0.497	1.000				
Mn	0.216	ND	0.673	0.711	1.000			
Ni	0.715	ND	0.735	0.206	0.518	1.000		
Pb	0.955	ND	0.838	0.088	0.335	0.695	1.000	
Zn	0.966	ND	0.764	-0.063	0.280	0.842	0.924	1.000
Carbonate fraction								
Cd	1.000							
Cr	0.499	1.000						
Cu	0.798	0.499	1.000					
Fe	0.683	0.474	0.977	1.000				
Mn	0.191	0.399	0.505	0.615	1.000			
Ni	0.796	0.827	0.727	0.687	0.549	1.000		
Pb	0.822	0.780	0.661	0.601	0.436	0.969	1.000	
Zn	0.721	0.330	0.937	0.891	0.263	0.552	0.470	1.000
Fe-Mn oxide fraction								
Cd	1.000							
Cr	ND	ND						
Cu	0.071	ND	1.000					
Fe	0.622	ND	-0.476	1.000				
Mn	0.466	ND	-0.511	0.906	1.000			
Ni	0.379	ND	-0.441	0.671	0.839	1.000		
Pb	0.350	ND	-0.217	0.520	0.506	0.722	1.000	
Zn	0.687	ND	-0.359	0.489	0.256	0.226	0.373	1.000
Organic fraction								
Cd	1.000							
Cr	0.484	1.000						
Cu	0.797	0.869	1.000					
Fe	0.679	0.804	0.819	1.000				
Mn	0.559	0.623	0.626	0.941	1.000			
Ni	0.649	0.794	0.819	0.960	0.936	1.000		
Pb	0.682	0.741	0.829	0.903	0.863	0.961	1.000	
Zn	0.805	0.806	0.955	0.799	0.640	0.787	0.795	1.000

Residual fraction								
Cd	1.000							
Cr	0.933	1.000						
Cu	0.891	0.979	1.000					
Fe	0.969	0.909	0.885	1.000				
Mn	0.947	0.865	0.845	0.980	1.000			
Ni	0.957	0.921	0.873	0.954	0.953	1.000		
Pb	0.957	0.969	0.962	0.960	0.952	0.951	1.000	
Zn	0.933	0.908	0.883	0.978	0.969	0.968	0.955	1.000

Correlation is significant at the level $p < 0.05$, Correlation is significant at the level $p < 0.01$. ND = Not Detected

4. Conclusion

Heavy metal concentrations in river water and sediments depend on not only industrial and domestic waste inputs but also on the geochemical composition of the area. The study reveals that there is a considerable variation in the concentration of heavy metals in water and sediments samples. These variations may be due to the change in the volume of industrial and sewage waste being added to river at different sampling stations. Most of the heavy metals viz., Cd, Cu, Mn, Ni, and Zn in Yamuna river water were found well below their respective BIS guideline value prescribed for Inland surface waters, Class-A, BIS (1982) during study period. Cr, Fe and Pb. Cr level in Yamuna water were found exceeding their BIS guideline value (0.05 mg/l) at S-2, S-8, S-9 and S-10 in the month of Jun., 03; Mar., 04, and Dec., 03 respectively. Iron level frequently exceeded the guideline value (0.3 mg/l) at most of the locations. Its presence in water, however, is due to its natural contents in soil and sediments. The concentration of Pb was found above the BIS guidelines value (0.1 mg/l) at S-3, S-7, S-8 and S-9 in the month of Dec., 04.

The concentrations of heavy metals in sediments were found considerably higher than those measured in river water. The metal pair ratios clearly reflects maximum enrichment of all studied metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) at in Yamuna river water site S-4 followed by site S-5 for Cd, Cr, Cu and Zn, while site S-6 for Mn, Ni and Pb. The geo-accumulation index comprised of seven grades (0 - 6), indicates various degrees of enrichment above the background values ranging from unpolluted to very strongly polluted sediment quality. Based on the geo-accumulation indices the Yamuna river sediments from S-1 to S-10 are considered to be unpolluted with respect to Cr, Cu, Fe, Mn, Ni and Zn. It is unpolluted to moderately polluted with Pb. In summer-03, the concentrations of Cd at S-4 (47.80 %), S-5 (44.51 %), and S-8 (47.57 %); Cr at S-8 (33.79 %); Ni at S-1 (38.17 %); Pb at S-7 (41.84 %), and S-8 (44.61 %); and Zn at S-4 (31.11 %), exist in either exchangeable or carbonate bound fractions. Whereas, in winter-05, the concentration of Cu at S-1 (33.63 %), S-3 (41.34 %), and S-7 (31.38 %); Ni at S-2 (31.52 %), S-4 (32.50 %), and S-8 D/S (33.06 %) was found in exchangeable fractions, and pose a high risk to the environment. According to RAC the concentrations of Cd and Pb at S-1 (56.79 and 51.81 %) exist in carbonate fraction in summer-03, while in winter-05 the concentration of Cu at S-2 (51.41 %) was associated with exchangeable

fraction are posing a very high risk to the aquatic environment. The Langmuir adsorption isotherm model as compared to the Freundlich model better fits the sorption data. Further, the nonlinear isotherm models better fit the data as compared to the linear ones. The monolayer capacity (Q^0) was calculated using the Langmuir adsorption isotherm for the activated carbons FAC, SAC, ATFAC, ATSAC, and ACF and was found to increase with increasing temperature, confirming the endothermic nature of the process. Also, the sorption capacity was found to be comparable to those of commercially available activated carbons and low-cost adsorbents used for the remediation of Cr(VI) from water/wastewater. The removal of Cr(VI) follows the order $ACF > FAC > ATSAC > ATFAC > SAC$. Overall, the activated carbon fabric cloth performed better than the other tested adsorbents. The rate of the adsorption is governed by a pseudo-second-order rate equation. Further, the adsorption of Cr(VI) is controlled by a particle diffusion mechanism in a majority of cases. The break through curve for adsorption of Cr(VI) in a column packed with activated carbon demonstrated that Cr(VI) was preferentially adsorbed and metal ion free effluent was produced. The desorption of Cr(VI) studied under similar conditions of flow rate, length and column diameter, etc. and observed that 120 ml of 0.1 N HNO_3 was sufficient for almost complete desorption of Cr. It can be concluded that the coconut shells/fibers commodity group will benefit from this research because it will add value to surplus byproducts. Carbon users would also be benefited because this material offers a viable alternative to coal based activated carbons. Thus, the studies presented here reveal that the derived low-cost activated carbons could be fruitfully employed as adsorbents for the removal of Cr (VI) and Cr(III) from water/wastewater without any sludge production.

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6. References

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