

Partitioning of Trace Elements in Different Components of a Highly Polluted Urban River Stretch in Delhi, India

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The study focuses on the partitioning of chromium, nickel, copper and lead among the components of the river Yamuna ecosystem (water, sediments, macrophytes and fish). The water is used for various purposes like irrigation, industrial, domestic and drinking. Almost zero dissolved oxygen and unacceptable levels of lead and phosphate pose a serious threat to the human and aquatic life. The concentration of the metals in the sediments is noticeably higher than that present at the reference site and the enrichment factors with respect to it vary from 0.60%–82.9% (Cr), 1.40%–90.5% (Ni), 1.00%–85.3% (Cu) and 3.80%–86.6% (Pb). The metal contents in the macrophyte (*Eichhornia crassipes*) and the fish (*Oreochromis niloticus*) are reasonably high and generally increase in the summers. The fish is not recommended for human consumption as it contains Cr, Cu and Pb above the permissible limits prescribed by FAO. One-way ANOVA indicates significant spatial variations in various parameters of water and sediments. The correlation analysis suggests a common source of some of the metals. Principal component analysis demonstrates that the domestic and industrial waste and coal fired thermal power plants contribute to the buildup of metal concentrations. On the basis of the findings some remedial measures are suggested.

Key words: *Fish, macrophytes, partitioning, sediment, urban river, water*

Introduction

The rivers play a major role in the economy of a country by sustaining agriculture, industry, energy generation and providing biological resources. With the expansion of human population and associated industries there is a concomitant increase in both, the resource utilization and the production of deleterious by-products and waste. The disposal of all kinds of wastes into the rivers, especially those in the industrial and urban areas, has led to a significant increase in a variety of inorganic and organic pollutants. Out of these pollutants, the heavy metals are of particular concern because of their persistent nature and undesirable concentrations in industrial and domestic wastes. Moreover, the metals are known for their bioaccumulative nature mainly due to their tendency to bind with protein molecules leading to subsequent cell division and prevention of replication of DNA¹⁻³.

In an aquatic system, the metals are transported to the sediments in substantial proportions through various processes thus affecting the neighboring groundwater. As a result of certain chemical and physical changes the sediments can release the trapped

metals to the overlying water leading to bioaccumulation. In order to understand the environmental impact of any aquatic body, it is essential to trace the dynamics of metals in all the major components of the system. This in turn will reflect on the processes responsible for the buildup of metals concentrations and the consequences thereof.

The river Yamuna is one of the important and largest tributaries of the river Ganges. The riparian states of the river are Himachal Pradesh, Haryana, Delhi and Uttar Pradesh. Delhi, the capital of India, is one of the important cities situated on the banks of the Yamuna. Approximately 86% of Delhi's total drinking water demand is met by this river⁴. In addition to this, the river water is used for irrigation, industrial and other allied practices. The stretch between Wazirabad and Okhla barrage in Delhi is only 2% of its catchment area but it contributes about 80% of the total pollution load of the entire river^{5,6}. The Yamuna has a very lean flow in summers. It may be important to mention here that the western bank is highly urbanized while the eastern bank is mainly influenced by the agricultural practices.

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Table 1 : Description of sampling sites.

S.N.	Station code	Name of sampling station	Activities
1	WBUS	Wazirabad Upstream	A, DW
2	WB-1 ^a	Soor Ghat	B, D, F, I
3	EB-1 ^a	Ram Ghat	B, D, F, I
4	WB-2	Najafgarh Drain Down Stream	D
5	EB-2	Najafgarh Drain Down Stream	A
6	WB-3	Income Tax Office(ITO)	D, B, I, T
7	EB-3	Income Tax Office(ITO)	A
8	ITODS	ITO Down Stream	A, T
9	WB-4	Okhla Head	B, F, R
10	EB-4	Okhla Head	A, F
11	WB-5	Okhla	B, D, F, I
12	EB-5	Okhla	A
13	OKHDS	Okhla Down Stream	A

^a EB and WB stand for the Eastern bank and the Western bank, respectively

A (Agricultural), B (Bathing), D (Domestic waste dumping), DW (Drinking water supply unit),

F (Fishing), I (Idol immersion), R (Recreational), T (Thermal Power Plant)

During the last two decades the river Yamuna has been a focus of a number of environmental studies. Most of these studies have been carried out on a single component namely water^{7,6}, sediment^{8,9} and macrophytes¹⁰. Only two reports^{11,12} are available where heavy metals in both water and sediments of the river Yamuna have been determined. In both of these surveys only three sites were selected in the large Delhi stretch of the Yamuna and the distinct environmental scenario of the East and the West bank was not considered. The available data on the pollution of the Yamuna may not be adequate to give the desired overall scenario of the degradation of the river. In view of the above a detailed study on the distribution of some heavy metals (Cr, Ni, Cu and Pb) in the different matrices namely water, surface sediment, free floating macrophyte and fish was carried out. The sampling was designed in such a manner so that a holistic picture of pollution and the difference in environmental degradation suffered by the East and the West bank emerges out. In order to arrive at some useful conclusion the data were analysed using multivariate statistical techniques.

The investigations will reflect on the partitioning pattern of the metals in different components of a flowing aquatic body receiving wastes from different sources. The study assumes a global significance because a large number of major rivers of the world are facing a similar situation where there is a lean flow

and the anthropogenic activities on the two banks are different. The results of the present study will help in gauging the status of pollution and identifying the main sources of pollution. This in turn will help in suggesting the remedial measures and change in the legislation if the need be. The findings may also provide vital information to different agencies engaged in restoring and preserving the water quality of the river Yamuna.

Materials and methods

Study area and site description

The river Yamuna is a major river of India originating from the Yamnotri glacier near Banderpunc Peak of the lower Himalayas (38°59'N 78°27'E) in the

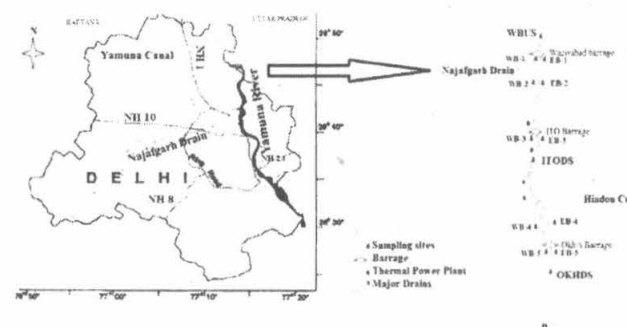


Fig. 1 : (A) Map (not as per dimensions showing (A) location of the Yamuna at Delhi and (B) Delhi stretch and the sampling stations

Table 2 : Analysis of CRMs of various samples

Metals	CRM-TMDW ^a (µg/mL)		IAEA-405 ^b (mg/kg)		NIST-1547 ^c (mg/kg)		NIST-1566a ^d (mg/kg)	
	Certified	Observed	Certified	Observed	Certified	Observed	Certified	Observed
Cr	0.02±0.0005	0.018±0.0014	84.0±3.94	79.6±5.71	1 ^e	0.94±0.088	1.43±0.46	1.40±0.26
Ni	0.06±0.0015	0.064±0.0040	32.5±1.4	30.6±2.4	0.69±0.09	0.72±0.06	2.25±0.44	1.86±0.14
Cu	0.02±0.0005	0.021±0.0009	47.7±1.2	44.6±4.11	3.70±0.40	4.0±0.16	66.3±4.3	62.0±3.44
Pb	0.04±0.0010	0.038±0.0012	74.8±2.20	69.9±2.8	0.87±0.03	0.84±0.04	0.37±0.01	0.31±0.02

^aCRM-TMDW (drinking water), ^bIAEA-405 (estuarine sediment), ^cNIST 1547 (peach leaves), and ^dNIST 1566a (oyster tissues) were used as CRMs of water, sediment, macrophytes and fish, respectively.

^e Indicative value

fluorite range at an elevation of about 6320m above sea level in the Uttarkashi District (Uttarakhand). After completing the mountainous course it enters the plains at Yamunanagar. It flows around 1370 km up to its point of confluence with Ganges at Allahabad. Its catchment area is spread over 366,220 km² and falls in even different states of India (Uttarakhand, Himachal Pradesh, Uttar Pradesh, Haryana, Delhi, Rajasthan and Madhya Pradesh). The Delhi stretch of the river Yamuna extends from Wazirabad in the North to Okhla in the South (Fig. 1). The two banks of the Yamuna, the East and the West, at Delhi have distinctly different anthropogenic activities. The East bank is mainly colored by agricultural fields except that a canal of the river Hindon which carries the industrial waste of western Uttar Pradesh falls into it¹³. On the other hand the West bank receives mainly domestic and industrial waste through 22 major and minor drains. Out of these drains Najafgarh drain is the largest and covers a distance of 51 km from its origin at Delhi Haryana border¹⁴. As the drain flows through Delhi several sub drains (about 70) carrying a variety of waste fall into it¹⁵. The small-scale metal based industries, located in the various parts of the city, release their waste into small drains that ultimately finds its way in the Yamuna. The lean flow of water adds to the inhomogeneity of the sampling. A usual feature of the Yamuna is that during the monsoon season the river gets flooded and the water and sediments are spread over a large flood plain area.

Thirteen sampling stations (Fig. 1) were selected in the Delhi stretch on the basis of drainage sites and other human activities as mentioned in Table 1. At three sites the samples were collected along the width (1/4, 1/2 and 3/4) of the river and homogenized. These sites were at the entrance (WBUS), in

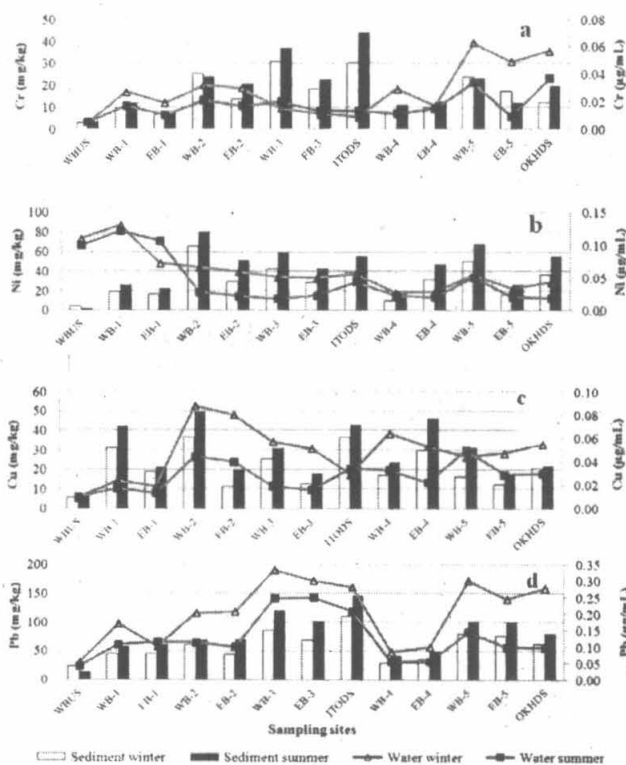


Fig. 2 : Concentrations of (a) chromium, (b) nickel, (c) copper and (d) lead in sediments and water

the middle (ITODS) and at the exit (OKHDS). These samples exhibit the extent of pollution of the Yamuna before entering Delhi, in the middle of the stretch and after leaving Delhi. Along with these, 10 samples from five places, one from the East bank and one from the opposite side on the West bank, were collected. Each of these samples was a composite of five replicates. The results of the analysis of these opposite points reflect on the differences in the extent of pollu-

Table 3 : Physicochemical characteristics of water in winter (W) and summer (S) seasons

SN	Sampling site	T(°C)		pH		TDS (mg/L)		DO (mg/L)		BOD (mg/L)		COD (mg/L)		SO ₄ ⁻⁻ (mg/L)		PO ₄ ⁻⁻ (mg/L)		NO ₃ ⁻ (mg/L)	
		W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S	W	S
		1	WBUS	22	27	7.4	7.4	307	507	5.5	4.8	1.9	6.3	7.1	18	20.0	30.0	-	0.02
2	WB-1	20	28	7.6	7.7	370	1037	1.8	2.2	4.2	5.3	18	24	62.1	69.2	0.38	0.28	5.81	5.55
3	EB-1	20	27	7.2	7.8	410	1098	2.0	3.0	3.3	8.7	15	29	56.2	56.2	0.02	0.21	1.61	4.74
4	WB-2	22	31	7.8	9.7	1077	1239	0.1	0.0	32	56	60	98	88.2	78.1	2.69	2.50	1.35	1.30
5	EB-2	22	30	7.8	9.9	1005	1311	0.1	0.1	29	52	49	98	100	99.3	3.16	3.19	3.30	2.98
6	WB-3	20	33	8.2	10.4	1065	1989	0.1	0.1	46	72	79	129	89.5	92.4	8.76	7.05	2.23	4.62
7	EB-3	18	31	8.2	9.8	1020	1899	0.0	0.0	21	54	37	108	93.7	95.0	8.74	6.75	2.26	4.44
8	ITODS	22	35	8.4	10.8	820	1017	0.1	0.0	58	89	97	134	112	89.8	9.87	7.49	2.36	11.5
9	WB-4	20	30	7.8	8.8	1020	1723	0.5	0.2	27	44	35	61	69.0	66.1	13.6	14.8	2.07	2.00
10	EB-4	20	30	7.6	7.9	1080	1811	0.3	0.3	21	39	38	51	73.7	73.1	5.83	13.5	1.79	2.17
11	WB-5	20	31	8.4	10	1080	1787	0.4	0.3	50	67	70	95	57.8	97.0	4.49	4.12	1.38	1.65
12	EB-5	18	28	8.0	8.9	890	1510	0.3	0.2	31	66	50	80	90.0	89.2	2.02	3.29	1.50	0.98
13	OKHDS	20	31	8.0	10.1	930	1207	0.2	0.2	58	74	103	111	52.3	95.1	2.28	4.99	1.28	9.72
Permissible limit		NA		6.5-8.5 ^a		500 ^a		4.0-6.0 ^a		6 ^b		10 ^b		250 ^a		0.10 ^a		10 ^a	

(-) below detection limit, NA-Not Applicable, ^aUSEPA, 2009a ^[29], ^bWHO^[33]

tion that the two banks of the river encounter The Wazirabad barrage upstream (WBUS) point where the Yamuna enters Delhi, was considered as the reference site.

Sample collection, preservation, preparation and analysis

Prior to use the labwares and polyethylene bags were kept in 10% (v/v) nitric acid solution for 24 hr, washed with double distilled water followed by rinsing with deionized water and dried in a dust-free environment. Samples of different components of the river was documented synoptically in winter (December, 2009) and summer (June, 2010) from 13 predecided sites. Due care was taken to collect the samples from a spot at least two meters away from the banks.

Water

The water samples at the depth of about 0.3 m were collected in high density polyethylene bottles and stored in an ice box until brought to the laboratory. The separate samples were collected for the determination of metals, anions and physicochemical parameters. For the analysis of metals in water the samples were preserved at pH=2 by the addition of nitric acid digested with a mixture of HNO₃ and HCl following the standard EPA 3010A method¹⁶ analyzed using ASV. The pH, TDS, DO (Winkler iodometric method), BOD (5-day) and CO (Open reflux method) were estimated following standard APHA methods¹⁷.

Sediments

The surface sediment samples (5-10 cm depth) were collected using a hand auger technique in acid treated polyethylene bags, sealed and immediately stored in an icebox until brought to the laboratory. The samples were dried in room temperature to a constant weight, powdered with mortar and pestle, sieved through 150 µm stainless steel sieve, packed in plastic bottle and finally stored at 4°C. The sieved sample were subjected to physicochemical analysis. The pH of the sediment suspension (1:2.5 w/v) was measured. The organic matter (OM, %, w/v) and the clay (%, w/w) content were determined by loss on ignition¹⁸ and hexametaphosphate methods, respectively. For the analysis of metals, one gram of each sample was digested using

Table 4 : General characteristics of sediments in winter (W) and summer (S)

SN	Sampling site	pH		OM (%)		Sand (%)		Silt (%)		Clay (%)	
		W	S	W	S	W	S	W	S	W	S
1	WBUS	6.5	6.7	0.23	0.38	92.1	89.2	7.30	10.3	0.56	0.44
2	WB-1	7.4	7.8	1.20	2.40	80.5	79.9	16.7	17.8	2.80	2.10
3	EB-1	7.4	7.5	1.80	2.00	81.5	87.3	16.3	11.1	1.80	0.90
4	WB-2	7.8	8.5	3.20	6.80	89.1	82.5	8.91	16.7	0.80	0.78
5	EB-2	7.5	8.0	3.10	7.20	90.3	88.9	8.30	10.1	1.20	0.92
6	WB-3	7.7	8.6	6.31	8.75	83.4	79.7	15.5	18.9	0.89	0.93
7	EB-3	7.2	8.0	4.02	7.67	85.3	80.4	13.5	18.3	1.40	1.10
8	ITODS	7.5	8.2	6.09	8.88	83.4	77.5	15.0	21.4	1.57	0.95
9	WB-4	7.6	8.1	2.99	4.39	73.3	75.4	25.2	23.5	1.20	0.79
10	EB-4	7.8	8.0	1.98	3.88	88.4	80.9	9.80	17.7	1.84	1.39
11	WB-5	7.7	7.9	3.45	5.55	80.8	80.1	15.4	16.3	3.48	3.33
12	EB-5	7.5	8.3	1.79	3.71	82.7	80.3	15.4	18.8	1.89	0.99
13	OKHDS	7.7	8.3	3.97	6.00	79.7	72.9	18.2	25.7	1.89	1.22

Table 5 : Concentration (mg/kg dry weight) of metals in macrophytes during winter (W) and summer (S)

Metals Sites	Cr		Ni		Cu		Pb	
	W	S	W	S	W	S	W	S
WBUS	1.79	2.92	2.11	2.80	24.3	32.7	6.71	12.3
WB-1	2.07	4.01	7.88	12.9	58.2	52.0	11.2	19.2
EB-1	1.94	3.55	6.25	10.3	31.3	41.1	10.4	31.6
WB-2	2.77	4.67	11.1	15.3	39.3	61.9	18.7	34.6
EB-2	1.92	4.44	8.32	11.0	40.4	58.2	20.6	36.5
WB-3	3.69	2.88	12.5	16.2	58.6	79.9	28.3	46.4
EB-3	2.08	5.09	5.19	8.81	40.0	62.5	22.3	36.5
ITODS	3.47	6.04	10.1	13.8	60.5	77.1	24.9	48.3
WB-4	2.10	5.84	7.32	10.4	39.4	49.1	14.5	28.7
EB-4	4.32	5.88	8.75	13.9	32.7	54.5	19.5	34.4
WB-5	8.29	18.7	5.30	13.3	52.2	84.2	32.5	49.7
EB-5	5.17	6.21	5.60	8.20	38.3	58.7	26.1	31.6
OKHDS	7.14	10.1	6.50	12.2	45.7	62.9	28.8	45.5

HNO₃, H₂O₂ and HCl on a hot plate following the standard procedure²⁰. After cooling, the sample was filtered and then diluted to 25 mL before analysis. In order to assess the anthropogenic contribution of metals to the sediments the percentage enrichment factor (%EF) was calculated using the formula^{21,22}:

$$\%EF = [(C - C_{min}) / (C_{max} - C_{min})] \times 100$$

Where C, C_{max} and C_{min} are the mean metal concentration (mg/kg) in the sediment and the maximum and minimum concentration (mg/kg), respectively.

Macrophytes

Composite samples of the macrophyte, *E. crassipes*, were collected from each site, washed with river water, sealed in polyethylene bags, transported to the laboratory in an ice box and finally stored in a deep freezer. The complete plant (shoot and root) was oven dried at 80 °C to a constant weight. The dried sample was crushed in a grinder, homogenized and subjected to acid digestion following the procedure suggested by Muller²³. 2 g of each sample was digested

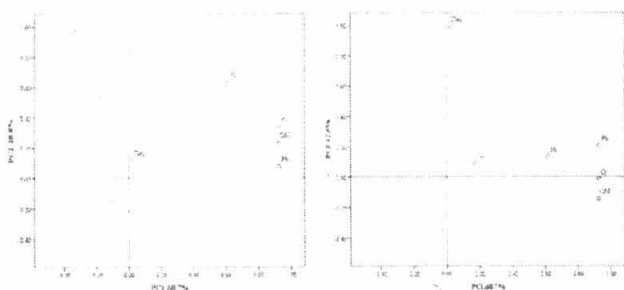


Fig. 3 : Loading plots of the variables on the space defined by PC1–PC2 and PC1–PC3

and the residue was dissolved in 10 mL of distilled water, filtered through a Whatman 42 filter paper and made upto 25 mL for analysis.

Fish

The level of pollution in the Delhi stretch of the river has reached to such a level that the fish are scantily visible. The only available species of the fish locally known as tilapia (*Oreochromis niloticus*) was collected. It was difficult to collect the fish from the predecided sites hence picked up from certain zones covering a number of sites. There is no objection in sacrificing the fish for experimental purposes as per the legal norms of the institute and the country. The fish, roughly of equal length and mass, were collected, packed in precleaned zip-lock poly bags and stored in ice box until brought to the laboratory to store in a deep freezer at -20°C . The sample was defrosted before analysis. The analysis of fish was carried out by following the procedure described elsewhere²⁴. The defrosted fish sample was weighed and ignited to ash. A weighed portion of the ash equivalent to 5 g fish was digested with HCl for 10 minutes, followed by slow addition of 5 mL of nitric acid. The solution was heated on a hot plate for 30 min. until yellow fumes started to appear. After cooling the solution was filtered and made upto 25 mL for analysis.

Reagents and instrumentation

All the reagents and chemicals were of analytical grade. The deionized water from a Milli-Q Millipore® 18.2M Ωcm^{-1} conductivity purification system (Bedford, MA, USA) was used throughout. For anodic stripping voltammetric (ASV) analysis supra pure grade chemicals from Merck (Darmstadt, Germany) were used. A portable pH meter (Lutron, PH-201) and a conductivity/TDS meter (Shimadzu 1100) were employed for the determination of pH and

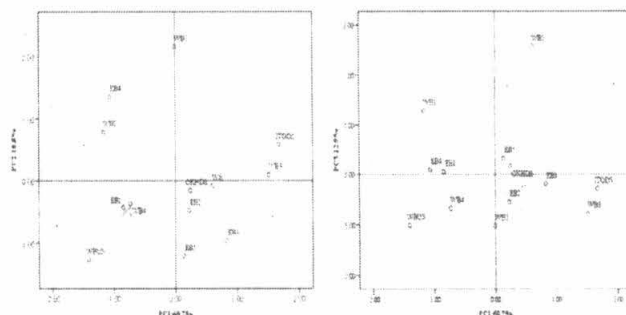


Fig. 4 : Score plots of the sites on the space defined by PC1–PC2 and PC1–PC3

TDS, respectively. The anions (Cl^- , NO_3^- and PO_4^{3-}) were analyzed on an Ion Chromatograph with 830 IC Interface, 819 IC detector, 833 IC Liquid Handling Unit, 820 IC Separation Centre, 818 IC Pump, 838 Advanced Sample Processor and IC Net 2.3 software (Metrohm, Switzerland). For the quantification of metals in sediments and biota, flame atomic absorption spectrometer (FAAS) (PerkinElmer, *AAnalyst 800*) was used. However, for the analysis of metals in water an ASV (Metrohm, Switzerland) with a differential pulse mode was used because of the need of a more sensitive technique. A multimode titrator (877 Titrino plus, Metrohm, Swiss made) was used to adjust the pH of water samples before ASV analysis.

The metal standards for calibration were prepared fresh every time by diluting the stock solutions (1000 mg/L, Merck) and the medium of the standards was kept the same as that of the digested samples. The CRMs closest to the material namely drinking water (CRM-TMDW) from high purity standards, estuarine sediment (IAEA-405), peach leaves (NIST 1547) and oyster tissues (NIST 1566a) were used for water, sediment, macrophytes and fish, respectively. The results assure that the accuracy of the adopted methods is within $\pm 10\%$ (Table 2). The values reported for all the parameters including metal ion concentration are an average of triplicate observations and the variance observed is less than 10%. The reagent blanks were run for the analysis of metals in water, sediment, macrophyte and fish and appropriate corrections made.

Data analysis

The statistical analysis of the collected data was performed using the SPSS 16.0 for Windows (SPSS Inc., USA) software. The single factor analysis of variance (ANOVA) was used to analyze the significant differences among the sampling sites for different

Table 6 : Concentration (mg/kg dry weight) of metals in fish during winter (W) and summer (S)

Metals	Cr		Ni		Cu		Pb	
	W	S	W	S	W	S	W	S
A (WBUS)	0.58	1.17	0.88	2.25	3.40	2.83	2.80	9.20
B (WB-1, EB-1)	5.68	11.4	8.54	8.21	15.2	11.74	11.7	28.6
C (WB-2, EB-2)	-	-	-	-	-	-	-	-
D (WB-3, EB-3)	-	-	-	-	-	-	-	-
E (ITODS)	-	-	-	-	-	-	-	-
F (WB-4, EB-4)	3.19	5.20	4.20	5.07	9.29	7.18	12.7	17.7
G (WB-5, EB-5)	4.54	6.60	5.57	10.6	13.3	12.0	14.5	23.4
H (OKHDS)	3.25	5.54	4.40	4.99	11.9	8.44	12.3	16.7
FAO limits	2.00		10.0		10.0		4.00	

(-) Indicates that the fishes were not observed at these sites

Table 7 : Sitewise enrichment factor (EF) for sediments and bioconcentration factor (BCF) for macrophytes

SN	Sampling sites	EF as compared to the least contaminated site				BCF			
		Cr	Ni	Cu	Pb	Cr	Ni	Cu	Pb
1	WBUS	0.60	1.40	1.00	3.80	471	23.2	3000	207
2	WB-1	18.9	26.0	70.5	29.0	138	82.1	2688	110
3	EB-1	9.6	22.4	32.4	29.9	189	91.9	2263	194
4	WB-2	52.6	90.5	85.3	38.7	140	282	766.7	169
5	EB-2	34.7	49.6	22.8	32.5	135	236	821.6	186
6	WB-3	75.1	62.9	51.1	67.5	188	417	1822	129
7	EB-3	42.1	43.2	21.7	54.4	299	192	1530	107
8	ITODS	82.9	58.1	77.0	86.6	432	48.2	2184	150
9	WB-4	15.7	15.7	32.9	16.8	199	354	912.4	311
10	EB-4	20.0	48.1	73.0	21.5	319	463	1162	350
11	WB-5	49.9	73.3	41.2	57.9	279	177	1451	185
12	EB-5	28.0	24.4	20.3	55.8	196	251	1276	168
13	OKHDS	31.6	56.8	35.1	43.6	184	297	1278	199

Table 8 : Spatial variations (one-way ANOVA) in metal concentrations in water, sediments and macrophytes

Metal	Water		Sediment		Macrophyte	
	F-value	P-value	F-value	P-value	F-value	P-value
Cr	$F=6.54$	$P < 0.01$	$F= 24.7$	$P < 0.01$	$F= 14.5$	$P < 0.01$
Ni	$F= 14.8$	$P < 0.01$	$F= 97.0$	$P < 0.01$	$F= 16.0,$	$P < 0.01$
Cu	$F= 4.71$	$P < 0.01$	$F= 34.2$	$P < 0.01$	$F= 8.4,$	$P < 0.01$
Pb	$F= 9.57,$	$P < 0.01$	$F= 80.2$	$P < 0.01$	$F= 18.1$	$P < 0.01$

Table 9 : Correlations between metal concentrations in different compartments and physicochemical parameters

	Cr(W ^a)	Ni(W)	Cu(W)	Pb(W)	Cr(S)	Ni(S)	Cu(S)	Pb(S)	Cr(M)	Ni(M)	Cu(M)	Pb(M)	OM%	Clay%
Cr(W)	1.00													
Ni(W)	-0.28	1.00												
Cu(W)	0.50	-0.67*	1.00											
Pb(W)	0.22	-0.32	0.22	1.00										
Cr(S)	0.12	-0.39	0.40	0.84**	1.00									
Ni(S)	0.48	-0.42	0.69*	0.59*	0.75**	1.00								
Cu(S)	0.05	-0.03	0.28	0.17	0.49	0.60*	1.00							
Pb(S)	0.20	-0.36	0.19	0.90**	0.89**	0.57*	0.31	1.00						
Cr(M)	0.84**	-0.29	0.29	0.28	0.22	0.44	0.03	0.33	1.00					
Ni(M)	0.18	-0.33	0.51	0.44	0.69**	0.74**	0.82**	0.48	0.05	1.00				
Cu(M)	0.41	-0.29	0.35	0.83**	0.88**	0.68*	0.48	0.85**	0.48	0.67*	1.00			
Pb(M)	0.57*	-0.66*	0.51	0.77**	0.77**	0.74*	0.24	0.80**	0.65*	0.54	0.81**	1.00		
OM%	0.14	-0.59*	0.52	0.83**	0.92**	0.71*	0.34	0.80**	0.17	0.66*	0.79**	0.81**	1.00	
Clay%	0.63*	0.16	0.00	0.20	0.05	0.22	0.20	0.22	0.75**	0.10	0.45	0.34	-0.07	1.00

^aThe alphabets W, S and M within the parenthesis indicate for water, sediment and macrophyte, respectively.

*Correlation is significant at the 0.05 level (df=24, critical value=0.388, 2-tailed).

**Correlation is significant at the 0.01 level (df=24, critical value=0.496, 2-tailed).

physicochemical parameters and concentration of metals in water, sediments and macrophyte. The correlation study was carried out using Pearson's correlation coefficient for the metals in different components. The principle component analysis (PCA) was done on the selected sediment properties and the measured heavy metals to understand the relationship among these variables and identify their origins.

Results and discussion

Physicochemical status of the Yamuna

The physicochemical characteristics of water and sediments are given in the Table 3 and Table 4. The pH values indicate a weak to moderate alkaline nature of the water. TDS is consistently higher at the downstream sites than that observed at the entry point (WBUS). The sulphate and nitrate concentrations in the water are below their permissible limits but the phosphate at most of the sites is above the limit. The phosphate concentration is significantly high as compared to that reported earlier in the Yamuna¹² and indicates an increase in the casual agricultural practices being followed. Almost zero dissolved oxygen at most of the sites in Delhi stretch clearly manifests the degraded state of the Yamuna. High values of TDS and phosphate are alarming for the aquatic life and the inhabitants of the surrounding slums. The differences in the values of most of parameters of the water on the eastern and the western bank are not specifically prominent. The level of BOD and COD are generally higher on the western bank. The high BOD and COD levels at the downstream sites are the indicators of the deterioration of the water quality due to the merging of different drains. If the seasonal variations in the physicochemical parameters of water are examined, generally, the values are higher in summer than in winter. A high evaporation rate and a lean flow of water in the river during the summer season lead to a rise in the values of various parameters. The significant spatial variations in the basic parameters are due to the localized activities.

The one-way ANOVA showed that the spatial variations in the river water are statistically significant for physicochemical

parameters namely pH ($F = 15.1$, $P < 0.01$), TDS ($F = 9.06$, $P < 0.01$), DO ($F = 61.7$, $P < 0.01$), BOD ($F = 38.8$, $P < 0.01$), COD ($F = 16.7$, $P < 0.01$), sulphate ($F = 6.21$, $P < 0.01$) and phosphate ($F = 12.6$, $P < 0.01$). The results represent significant spatial variations in most of the parameters. The spatial fluctuations in the characteristics of the sediments are also significant for pH ($F=11.2$, $p<0.01$), OM ($F=28.6$, $p<0.01$), sand ($F=6.32$, $p<0.01$), silt ($F=5.57$, $p<0.01$) and clay ($F=25.7$, $p<0.01$). The sediment characteristics vary to a small extent in the two seasons. However, organic matter is generally higher in summers.

Dynamics of the metals

An attempt has been made to understand the distribution of metals (Cr, Ni, Cu and Pb) in different compartments of the river with spatial and seasonal factors influencing it. The concentrations of metals (winter and summer) in water and sediments at different sites are given in the Fig. 2. The concentrations of metals in biota for the two seasons are given in Table 5 and Table 6.

Chromium

Chromium in the river water ranges from 0.01 to 0.06 $\mu\text{g}/\text{mL}$ and in sediments from 2.84 to 44.0 mg/kg (Fig. 2). If the level of chromium in the sediment at the least contaminated site is taken as the reference, the enrichment, 0.60%–82.9% (Table 7), suggests that during the stretch of flow there is an appreciable contribution of Cr from the various sources. The accumulation of chromium in the macrophyte is not very pronounced but there is a significant seasonal variation (Table 5) and Cr content increases in the summer. The Cr content in the fish (Table 6) is generally above the permissible limit (2 mg/kg)²⁵. A noticeable rise in Cr concentration in the fish is observed in the summer as compared to that in winter.

Nickel

Nickel concentrations vary between 0.02 to 0.13 $\mu\text{g}/\text{mL}$ in water column and over a wide range of 2.08 to 79.9 mg/kg in sediments (Fig. 2). Taking the least contaminated site as a base, an enrichment of Ni in sediments, 1.40% to 90.5% (Table 7), indicates an appreciable contribution of nickel from different sources to the system. The macrophyte shows a moderate accumulation of nickel with a noticeable seasonal variation (Table 5). Generally, the nickel content in the fish (Table 6) is within the permissible limit (10 mg/kg)²⁵. Unlike Cr, the nickel content in the fish

does not show noticeable increase in the summer season.

Copper

The concentrations of copper in the aqueous phase range between 0.01 to 0.09 $\mu\text{g}/\text{mL}$. The sediment bound Cu varies over a wide range from 5.63 to 49.7 mg/kg (Fig. 2). The percent enrichment factor of copper varies from 1.00 to 85.3 (Table 7) which reflects on the anthropogenic contribution of copper within Delhi. This may be attributed to the dumping of domestic waste from various drains. The *E. crassipes* shows an exceptional tendency to accumulate copper with bioconcentration being more pronounced in the summer at most of the sites (Table 5). At the zones B, G and H (Table 6) the level of copper in the fish is slightly above the permissible limit (10 mg/kg)²⁵. If the seasonal variation in the level of copper in fish is observed it shows a different pattern; being lower in summers. No suitable explanation can be offered for this inconsistent behaviour of copper.

Lead

Like the other metals, lead shows a large spatial variation, both in water (0.04 to 0.33 $\mu\text{g}/\text{mL}$) and sediments (13.2 to 146 mg/kg) (Fig. 2). The high enrichment factor varying from 3.80% to 86.6% (Table 7) suggests a major source contributing lead. A maximum lead enrichment (86.6%) is observed at ITODS which may be attributed to the effluents and particulate matter released from the nearby coal fired thermal power plants. In this regard the contribution of heavy vehicular load in the adjoining area cannot be ignored. The bioconcentration of lead in *E. crassipes* is reasonably high and increases in the summer (Table 5). The lead content of the fish collected from various zones is above the permissible limit (4 mg/kg)²⁵, (Table 6) making it unfit for human consumption. Like Cr, the level of lead in the fish increases in the summers.

From the foregoing discussion it is clear that the river Yamuna is severely polluted. The enrichment factor values (Table 7) indicate that the deterioration of Yamuna is significantly high on the western bank as compared to that on the eastern bank. Partition coefficients ($K_d = [M_{\text{sediment}}]/[M_{\text{water}}]$) are high ranging from 337 to 3361 (Cr), 30.4–1612 (Ni), 201–1790 (Cu) and 311–542 (Pb). High K_d values indicate the tendency of these metals to be associated with the solid phase. The metal loaded sediments can pose threat to the ecosystem as the metal may release into the

overlying water on certain changes in the environmental parameters.

The macrophyte, *E. crassipes*, is reported to be a good sorbent of the metals²⁶ and the increase in the uptake with the temperature is on the expected lines^{27,28}. The higher uptake capacity of *E. crassipes* for all the four metals is indicated by the bioconcentration factors (Table 7). The high bioconcentration factor for the macrophyte, *E. Crassipes*, suggests that it can be used for phytoremediation. A comparison of the metal concentrations found in the fish of Yamuna and the permissible limits proposed by Food and Agriculture organisation²⁵ indicates that Cr and Pb contents are significantly high in both the seasons and the consumption of fish may be detrimental (Table 6). However, the copper content exceeds the permissible limit at few sites whereas nickel is generally below the permissible limits.

The spatial variations in the metal concentrations in water, sediment and macrophyte are statistically significant and are given in Table 8. In this context it may be pertinent to mention that the sediments are the actual indicators of metal enrichment in any water body. As expected the spatial variations are more pronounced in the case of sediments. Among the metals the spatial fluctuations are more apparent for nickel and lead. If a comparison is made of the corresponding sites on the East and the West bank the concentrations of all the four metals in water are generally high at the western bank. This effect is more noticeable in the sediments as indicated by the enrichment factor (Table 7). The enrichment of the metals in the sediments at the downstream sites is noticeably higher than that at the reference site. The enrichment is more pronounced at the western bank than that at the eastern side. The exception to the trend are the sites EB-4 and WB-4 where the order is reverse due to the confluence of the Hindon canal at the eastern bank.

From the above discussion it is apparent that the metals entering into the water phase from the different sources are getting distributed in the other phases. During the flood in the monsoon season the metal loaded sediments are spread all over the flood plain area and contaminate the soil. The metals from the contaminated soil may enter into the food chain through agricultural produce. The river water as such is being used for drinking by the inhabitants of the nearby slums. Thus it is relevant to assess the domain level of contamination and the probability of the risk

due to the metals enriched in water and sediments. Viewing the data of water in the light of the criteria set by United States Environmental Protection Agency for fresh water²⁹, Ni touches the upper limit at the WBUS, WB-1, and EB-1, whereas Pb crosses the limit at all the sites and can pose a serious threat to the ecosystem. If the data are examined in the light of other criteria³⁰, copper and lead with the exception of the reference site are generally above the criteria maximum concentration (CMC), 0.013 µg/mL Cu and 0.063 µg/mL Pb, and can cause acute toxicity to the aquatic life. On the other hand, the aquatic life seems to be unaffected with regard to Cr as it is below the criteria continuous concentration (CCC, 0.074 µg/mL) whereas the nickel crosses the CCC limit (0.052 µg/mL) at the sites in the proximity of the entry point. In the case of sediments, at most of the sites, chromium falls under the less toxic category (<25 mg/kg)³¹ and nickel in the moderately toxic level (20-50 mg/kg). Copper possesses a moderate toxicity (25-50 mg/kg) at almost half of the sites WB-1, WB-2, WB-3, ITODS EB-4 and WB-5 (summer) and at the remaining site it is at a less toxic level (<25 mg/kg). At some of the sites, WB-2, WB-3, ITODS (summer), WB-5 and OKHDS (summer) concentration of nickel rises to a severely toxic level (>50 mg/kg). The level of lead at most of the sites is more alarming as it falls in the range of severe toxicity (>60 mg/kg).

If TEL (threshold effect level)/PEL (probable effect level) criteria³² is used for the risk assessment Cr seems to be safe (below TEL, 37.3 mg/kg), Cu may cause threat to the aquatic life occasionally as it exceeds TEL (35.7 mg/kg) at WB-1, WB-2, ITODS and EB-4 in the summer. Toxic effects due to Ni and Pb would frequently be visible on the aquatic life as their values fall above the PEL (36 mg/kg for Ni and 91.3 for Pb) at several sites.

Multivariate statistical analysis

The Pearson's correlation coefficients among the metal concentrations in different components and sediment properties are shown in Table 9. A positive correlation between the concentrations of Pb in water and sediments shows some relationship exists between the lead species in the two phases. Positive correlations observed between Cr-Ni ($r=0.75$, $p=0.01$), Cr-Pb ($r=0.89$, $p=0.01$), Ni-Cu ($r=0.60$, $p=0.05$) and Ni-Pb ($r=0.57$, $p=0.05$) in the sediments are the indicators of common anthropogenic sources of these metals. It is likely that these metals are being contributed by small scale metal finishing industries.

Chromium, nickel and lead content in the sediments show a significant and positive correlation with the organic content of the sediments. This indicates that the said metals may be settling down by adsorption or forming complex with the organic matter. A high, positive and significant correlation observed between aqueous and macrophyte bound chromium and lead indicates that these metals are bio-accumulating in the macrophytes. Correlations like Cr in water and Pb in macrophyte and Cu in the water and Ni in sediments and Pb in water and Cu in macrophyte are difficult to explain.

The PCA was conducted on the selected sediment properties and the measured heavy metals. Three principal components with eigenvalues greater than or near 1 were extracted. These three components account for about 92% of the total variance and play an important role in explaining the contamination due to heavy metals and their sources (Fig. 3). To illustrate the contribution of the different variables and the samples to individual principal components, the distribution of the loads and the object scores in the PC1-PC2 and PC1-PC3 axis is shown in Fig. 3 and Fig. 4. The results (Fig. 3) demonstrate that the first principal component (PC1) accounts for 60.7% of the total variance and has a high loading of Cr, Pb and OM and a moderate loading of Ni. This observation supports the results inferred by correlation analysis. The close relationship between Cr, Ni, Pb and OM suggests that they are being contributed by the same source. The common source may be municipal wastewater, sewage and industrial effluent. The second component (PC2) accounts for 18.8 % of the total variance, with a high loading of Cu and a moderate loading of Ni. This also indicates towards a common source of the two metals. The third principle component (PC3) contributes 12.9 % to the total variance and has a high loading of clay only indicating a distinct pattern of clay.

As shown in Fig. 4, the sites EB-5, EB-2, OKHDS, WB-5, EB-3, WB-3 and ITODS display positive values for PC1, leading us to conclude that the main source of Cr, Ni, Pb and OM in the sediments is the domestic and industrial waste dumping and to some extent the agricultural runoff containing metal contaminated soil. The sites WB-3, ITODS, WB-1, WB-2 and EB-4 present positive values for PC2 and show the loading of Ni and Cu. The nickel and copper pollution at these sites can possibly be due to fly ash from the nearby thermal power plants (WB-3, ITODS),

religious rituals like idol immersion (WB-3, WB-1), merger of the river Hindon (EB-4) and Najafgarh drain (WB-2). The sites EB-1, EB-4, OKHDS, EB-5, WB-1 and WB-5 present positive score values for PC3, which corresponds to a high loading of clay. Among these, the sites on the eastern bank and OKHDS, receive runoff from the agricultural fields which might be contributing to clay content. On the other hand probably idol immersion activity is leading to elevated level of clay at WB-1 and WB-5.

Conclusions

The study reveals that the Delhi stretch of the Yamuna is severely polluted. The dissolved oxygen is almost zero at most of the sites. The levels of BOD, COD, phosphate and lead in water are alarming. The metals are highly concentrated in the sediments from which they can leach into the overlying water as a result of environmental perturbation. The metals are also accumulating in the biota and the fish may not be safe for the human consumption. Significant spatial fluctuation in the level of pollution both in water and sediment is indicated by ANOVA. This may be attributed to the site specific activity including the confluence of different drains and a lean flow of water for most of the time of the year. Sites on the western bank are distinctly more polluted which may be attributed to a large number of drains merging in the river Yamuna on the western side. The correlation study suggests that either some of the metals have a common source or get mixed in the drains receiving waste from various metal based industries. It is difficult to identify any specific activity leading to pollution but the main contributors are Najafgarh drain, coal fired thermal power plants and the river Hindon. Strict laws already exist to curb the pollution but they need to be effectively implemented. More treatment plants have to be installed and the plants operating under efficiency are to be upgraded. The small scale industries located in various areas should be connected to common treatment plants to ensure that no effluent enters Yamuna without treatment. The metal loaded macrophytes stacked at the banks are either consumed by cattle or incinerated there. They will either contaminate the milk or enter into the river in the ash form leading to recontamination. The macrophytes should be properly disposed or can be used for biogas production. The soil and the agricultural produce of the flood plain area should be regularly monitored for the heavy metal contents.

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33. WHO (World Health Organization), WHO Handbook, Genawa (1986).Table 1 : Description of sampling sites.