Heavy metal pollution in freshly deposited sediments of the Yamuna River (the Ganges River tributary): a case study from Delhi and Agra urban centres, India

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Abstract The Yamuna River sediments, collected from Delhi and Agra urban centres, were analysed for concentration and distribution of nine heavy metals by means of atomic adsorption spectrometry. Total metal contents varied in the following ranges (in mg/kg): Cr (157–817), Mn (515–1015), Fe (28,700–45,300), Co(11.7–28.4), Ni (40–538), Cu (40–1204), Zn (107–1974), Pb (22–856) and Cd (0.50–114.8). The degree of metal enrichment was compared with the average shale concentration and shows exceptionally high values for Cr, Ni, Cu, Zn, Pb and Cd in both urban centres. In the total heavy metal concentration, anthropogenic input contains 70% Cr, 74% Cu, 59% Zn, 46% Pb, 90% Cd in Delhi and 61% Cr, 23% Ni, 71% Cu, 72% Zn, 63% Pb, 94% Cd in Agra. A significant correlation was observed between increasing Cr, Ni, Zn, and Cu concentrations with increasing total sediment carbon and total sediment sulfur content. Based on the Müller's geoaccumulation index, the quality of the river sediments can be regarded as being moderately polluted to very highly polluted with Cr, Ni, Cu, Zn, Pb and Cd in the Delhi and Agra urban centres. The present sediment analysis, therefore, plays an important role in environmental measures for the Yamuna River and the planning of these city centres.

Keywords Heavy metals · Yamuna River · Sediment pollution · Ganga Plain

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Introduction

Urbanisation and freshwater rivers are inextricably linked with environmental issues. In the name of urban development, anthropogenic activities are continuously modifying the chemical composition of a river system. Life depends upon the availability of chemical elements in the right proportions and combinations. Elements such as heavy metals are essential elements for life in normal concentrations, but are toxic when present in higher concentrations in any component of environment because of their potential toxicity to micro-organisms, plants and animals. In a river system, sediments are an important source for assessing heavy metal pollution in rivers, as they have a long residence time (Förstner and Wittmann 1983; Müller and others 1979). Considerably high metal levels in water and sediments of the Yamuna River have already been reported (Ajmal and others 1985; Subramanian and others 1987). These earlier studies were restricted either to a few sampling stations or bulk sediment analysis without considering grain size. In the present study, Yamuna River sediments from Delhi and Agra urban centres were analysed to establish the concentration and distribution of nine heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd) in order to understand the effects of human action on the quality of river sediments.

Study area

The 1000-km-long Yamuna River originates in the Himalayan mountains as a main tributary of the Ganges (Ganga) River. After descending through the Himalaya, the river passes through the capital city of India, Delhi, meanders through Agra and joins the Ganges River at Allahabad. River hydrology is highly dependent upon the monsoon climate and characterised by very low flows in the pre-monsoon season (summer) and extremely high flows during the monsoon season. The river deposits its sediments in the form of mid-channel bars, point bars, natural levees and floodplains just after the monsoon season. These geomorphic units are cultivated after the monsoon season by the local people. The river sediments contain 3.5–5.2% $CaCO_3$ and 0.7% organic matter (Ajmal and others 1985). The river water is basic in nature (pH 7.4–7.6) with high total dissolved solids ranging between 260 and 1340 mg l^{-1} (Pachauri and Sridharan 1998). Delhi and Agra urban centres alone contribute a disproportionate 78% of the total population load in the Yamuna River basin but constitute only 2.4% of the river length. This high population load generates a large volume of urban effluents, including industrial, domestic and municipal waste, which flows directly into the river through several open drainage systems. A stretch of the Delhi River alone receives about 17,000 million l of urban effluents daily from 17 drains criss-crossing the city. These urban effluents can modify the geochemical characteristic of river sediments which may affect millions of people living in the area.

Methodology

Sample collection, choice of sediment size

A 30-km-long stretch of the river in Delhi and 15-km-long in Agra were selected for the present study. A total of 31 freshly deposited surface sediment samples were collected during the dry months of 1993 in the post-monsoon period (Fig. 1). Samples of the first 5–10 cm of the river deposits were taken from the middle or the banks of the active river channel. Higher quantities of metals generally accumulate in the fine-grained sediment fractions because of the higher surface-area to grain-size ratio (Gibbs 1973). A grain-size fraction comprising fine silt and clay would be fine enough to accumulate higher quantities of heavy metals in the river sediments. The sediment size fraction down to 20 μm (medium silt to clay) was used in this study in order to minimise the grain-size dependencies of metal concentration.

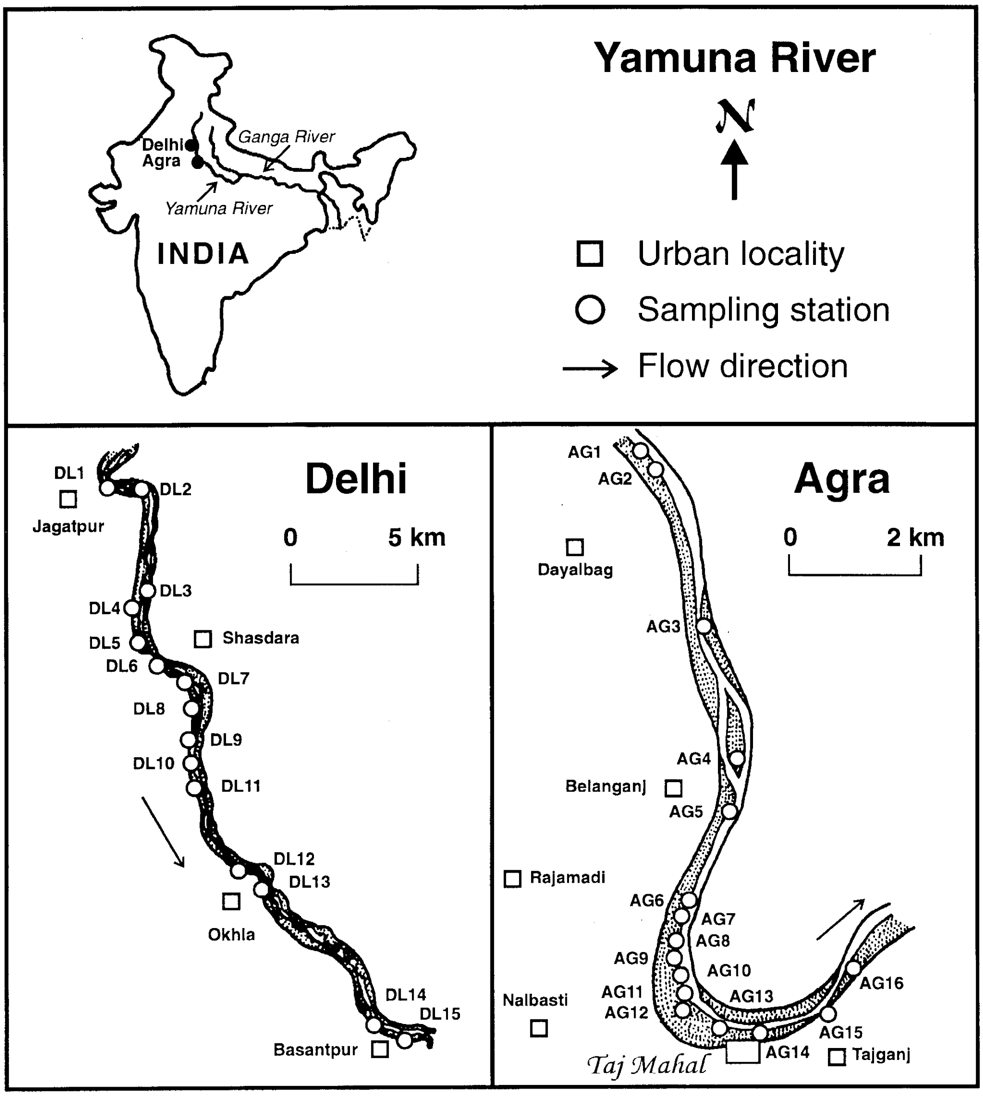

Fig. 1
Location map of the study area showing sampling sites in Delhi (*D1–D15*) and Agra (*A1–A16*) urban centres

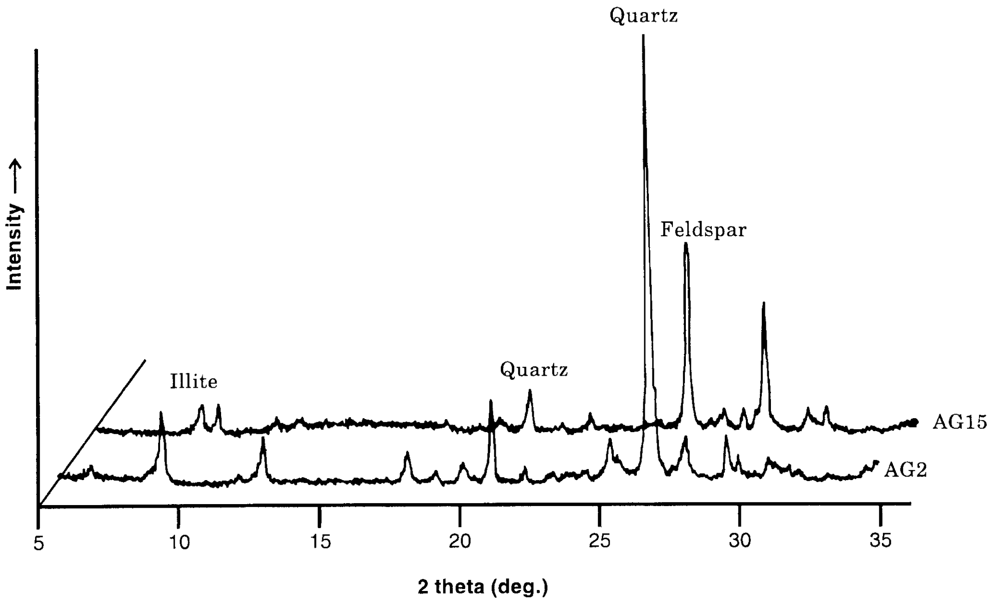

Fig. 2
XRD analysis of the Yamuna River sediments (*A2* and *A15*)

Granulometric and mineralogical analysis

The granulometric and mineralogical analysis provides basic information for the geochemical investigations of river sediment. The required granulometric fraction was separated from the collected sample by a mechanical wet-sieving method. In order to avoid sample contamination, nylon sieves and distilled water were used. The qualitative mineralogical analysis was done by a Siemens D500 Diffractometer.

Chemical analysis

The total digestion method was used to determine heavy metal concentrations in the river sediments (Jackwerth and Würfels 1994; Ruppert 1987). A 100-mg sieved sediment sample was heated with perchloric acid, nitric acid and hydrofluoric acid in closed Teflon beakers at 150 °C for 5 h and fumed at 180 °C for about 11 h. The solutions were directly analysed for heavy metals by flame- and graphite-furnace methods with the Perkin-Elmer Atomic Absorption Spectrophotometer models 3030 and 4100. Total sediment carbon and sulfur were also analysed using the Carbon and Sulfur determination model CS-225, LECO Corporation, USA. For quality control, the standard STSD-3, analytical blanks and duplicates were analysed using the same procedures and reagents. Care was taken during sampling, handing and analysis to prevent the samples coming into contact with dust and metals. The comparison of certified values and analytical values indicates no significant difference for most metals and analytical results are acceptable (Singh 1996).

Results and discussion

Nature of sediments

The Yamuna River sediments are mainly composed of very fine sand, silt and clay derived from the Himalayan region. Granulometric analysis shows that the <20-μm

Table 1
Statistical parameters for heavy metal concentrations (in mg/kg) in the Yamuna River Sediments from Delhi and Agra urban centres

Statistical Parameters	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
Delhi									
Minimum	163	515	29,200	13.0	40	40	110	22	0.5
Maximun	817	1015	45,300	28.4	538	829	1472	253	11.8
Average	394	695	40,500	18.0	159	275	561	76	4.5
Median	303	695	41,200	16.7	69	171	232	37	3.0
Agra									
Minimum	157	595	28,700	11.7	54	43	107	24	1.1
Maximum	469	965	42,900	23.5	180	1204	1974	856	114.8
Average	263	718	37,700	18.7	101	339	554	168	32.5
Median	233	713	37,600	19.0	88	154	338	54	5.2

Table 2
Ratios of heavy metal concentrations in the Yamuna River sediments of Delhi (D1–D15) and Agra (A1–A16) urban centres to average shale background

Sample	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
D1	1.8	0.7	0.9	0.9	0.7	0.9	1.2	1.1	1.7
D2	2.1	0.8	0.8	0.9	0.6	1.1	1.5	1.9	5.1
D3	7.5	0.8	0.8	0.8	1.7	3.8	2.4	2.7	17.5
D4	2.0	1.0	0.8	0.8	0.7	0.9	1.2	1.2	4.1
D5	8.5	1.2	1.0	1.5	8.0	14.0	11.4	5.3	39.3
D6	4.1	0.7	1.0	1.0	3.3	7.6	6.0	5.8	20.5
D7	4.2	0.8	1.0	1.1	3.2	9.3	6.1	2.7	29.8
D8	3.0	0.8	0.9	0.9	0.8	1.5	1.7	1.7	4.4
D9	2.8	0.9	1.0	1.0	0.8	1.2	2.0	1.6	3.2
D10	2.5	0.9	0.6	0.7	0.9	7.9	9.3	12.7	10.1
D11	9.1	0.9	0.9	1.3	4.9	18.4	13.9	1.5	25.3
D12	3.4	0.8	0.9	1.1	1.0	1.5	1.9	1.7	1.8
D13	2.6	0.6	0.8	0.9	0.9	1.1	1.7	1.5	5.3
D14	6.4	0.6	0.8	0.7	3.9	11.6	15.5	7.8	29.1
D15	5.7	0.7	0.8	0.8	3.6	10.6	12.9	8.1	28.3
A1	1.8	1.0	0.9	1.1	1.5	1.4	1.8	1.5	19.7
A2	2.1	0.9	0.9	1.1	1.2	1.3	1.7	1.8	11.9
A3	1.8	0.8	0.8	0.9	1.1	1.1	1.2	1.3	5.6
A4	2.0	0.9	0.9	1.2	0.8	1.0	1.3	1.2	3.7
A5	2.2	1.1	0.8	0.9	1.0	1.1	1.1	1.3	6.1
A6	1.7	0.9	0.8	1.1	1.0	1.4	1.5	1.4	11.8
A7	2.1	0.8	0.9	1.0	0.8	1.2	1.5	1.4	5.3
A8	2.2	0.8	0.8	1.0	0.9	2.1	2.3	1.7	13.7
A9	3.4	0.8	0.8	1.0	1.0	6.3	54	3.6	14.9
A10	3.0	0.7	0.9	1.0	1.8	4.7	4.8	5.1	31.5
A11	3.6	0.7	0.8	1.0	2.2	9.6	6.0	42.8	149.0
A12	3.1	0.9	0.9	1.1	1.4	8.2	5.4	11.3	188.8
A13	5.0	0.7	0.7	0.8	2.5	26.8	20.8	20.6	382.7
A14	5.2	0.9	0.6	0.6	2.7	26.2	19.6	16.4	370.7
A15	4.2	0.7	0.7	0.9	1.9	15.4	10.1	12.6	270.7
A16	3.5	0.8	0.8	1.0	2.0	13.1	8.8	11.1	248.0

fraction (medium silt to clay) in the total river sediment ranges from 4 to 77% in Delhi and from 5 to 42% in Agra. These variations are due to different positions of sediment samples in the river depositional units, i.e. flood plain, mid-channel bar and top of the channel bars, etc. X-ray diffraction analysis of samples A2 and A15 shows the presence of quartz, feldspar and illite minerals in bulk mineralogical composition (Fig. 2).

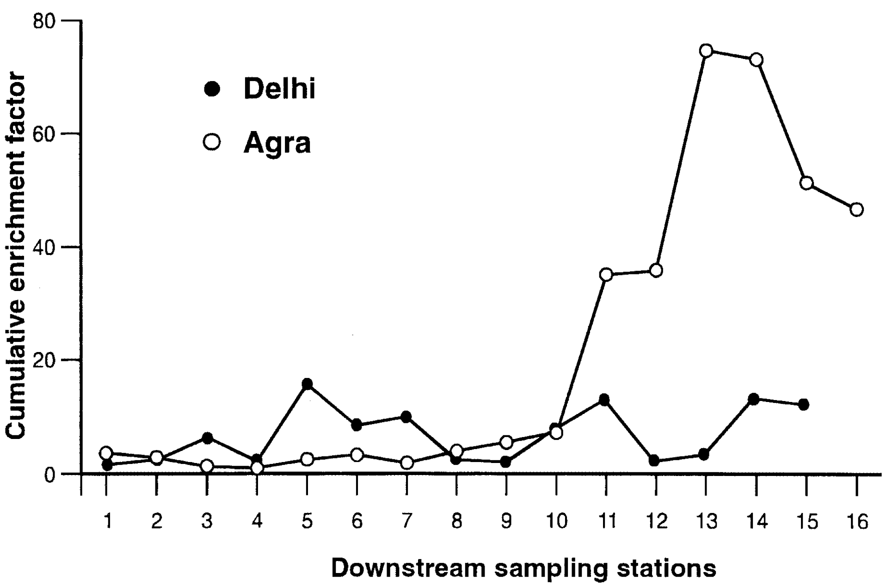

Fig. 3
Downstream variation in cumulative heavy-metal enrichment in the Yamuna River sediments (<20-μm fraction) of Delhi and Agra. The upstream sampling point is the entry of the river into an urban centre

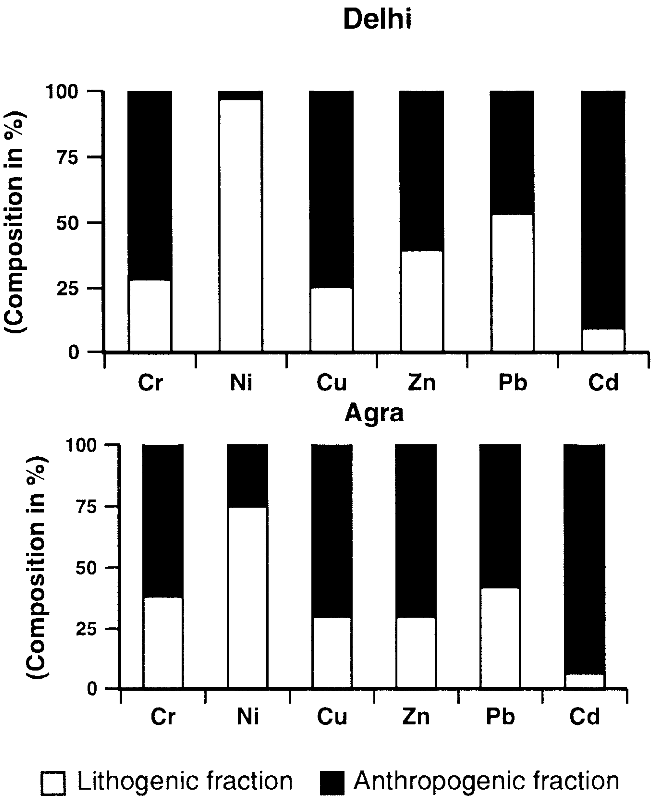

Fig. 4
Percentage composition of lithogenic and anthropogenic fractions of heavy metals in the Yamuna River sediments

Heavy metals in sediments

Heavy metal concentrations and their distribution in the Yamuna River sediments show varying and different behaviour. The metal concentrations were found in the following ranges (in mg/kg): Cr (157–817), Mn (515–1015), Fe (28,700–45,300), Co (11.7–28.4), Ni (40–538), Cu (40–1204), Zn (107–1974), Pb (22–856) and Cd (0.50–114.8). The minimum, maximum, average and median values for these heavy metals are presented in Table 1. The maximum Cr, Mn, Fe, Co, and Ni levels were detected at Delhi, whereas the maximum Cu, Zn, Pb and Cd levels were detected at Agra. The heavy metal concentration in average shale is the worldwide standard and is used as a reference for uncontaminated sediments (Turekian and Wedepohl 1961). Quantification of heavy metal enrichment was expressed by the metal ratio with respect to average shale. Metal ratios for the river sediments show various degrees of enrichment (Table 2). The values are greater than one except for Mn, Fe and to some extent for Co. High ratios of Cr, Ni, Cu, Zn, Pb and an exceptionally high ratio of Cd for some sediment samples have been recorded. In particular, a high Pb ratio at the D10 location was attributed to the atmospheric deposition of aerosols containing Pb from the nearby highway in Delhi. These high metal ratios indicate the anthropogenic source of heavy metals in the river sediments. The lower values of the Fe and Mn ratios may be due to the fact that the oxides may provide adsorbing sites for other metals.

To see the cumulative effect of heavy metal distribution, the average shale concentration is brought back to 100. Thus, the total average shale concentration for Cr, Ni, Cu, Zn, Pb and Cd metals will be 600, which acts as a base level for the presentation of the cumulative enrichment. The total concentrations of these six metals were calculated for each sample. The cumulative enrichment factors were evaluated after subtracting and then divided by 600. Figure 3 presents the longitudinal variation in these commutative heavy metal enrichment values in the river sediments. The Delhi shows three prominent peaks, indicating 10–15-fold enrichment within a 30-km-long stretch of river . In a 15-km-long stretch of the river Agra, the cumulative enrichment factor extends from base level to highest level (>50 times) of the study area. Such a high enrichment factor can be explained by the massive discharge of heavy metal-rich urban effluents along with the high adsorption capacity of the river sediments.

A river has two sources of heavy metals: lithogenic sources from weathering of rocks and anthropogenic

Table 3
Interelement relationship in the correlation coefficient matrix of the Yamuna River sediments. Significant at 90% probability, 31 samples

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd	C	S
Cr	1										
Mn	−0.04	1									
Fe	0.07	0.18	1								
Co	0.10	0.50	0.69	1							
Ni	0.84	0.13	0.22	0.36	1						
Cu	0.66	−0.18	−0.41	−0.18	0.60	1					
Zn	0.67	−0.24	−0.44	−0.27	0.63	0.96	1				
Pb	0.18	−0.26	−0.44	−0.25	0.18	0.55	0.50	1			
Cd	0.23	−0.21	−0.54	−0.30	0.17	0.81	0.69	0.64	1		
C	0.58	−0.07	−0.60	−0.28	0.56	0.80	0.86	0.51	0.53	1	
S	0.78	0.18	−0.13	0.12	0.81	0.65	0.68	0.25	0.25	0.76	1

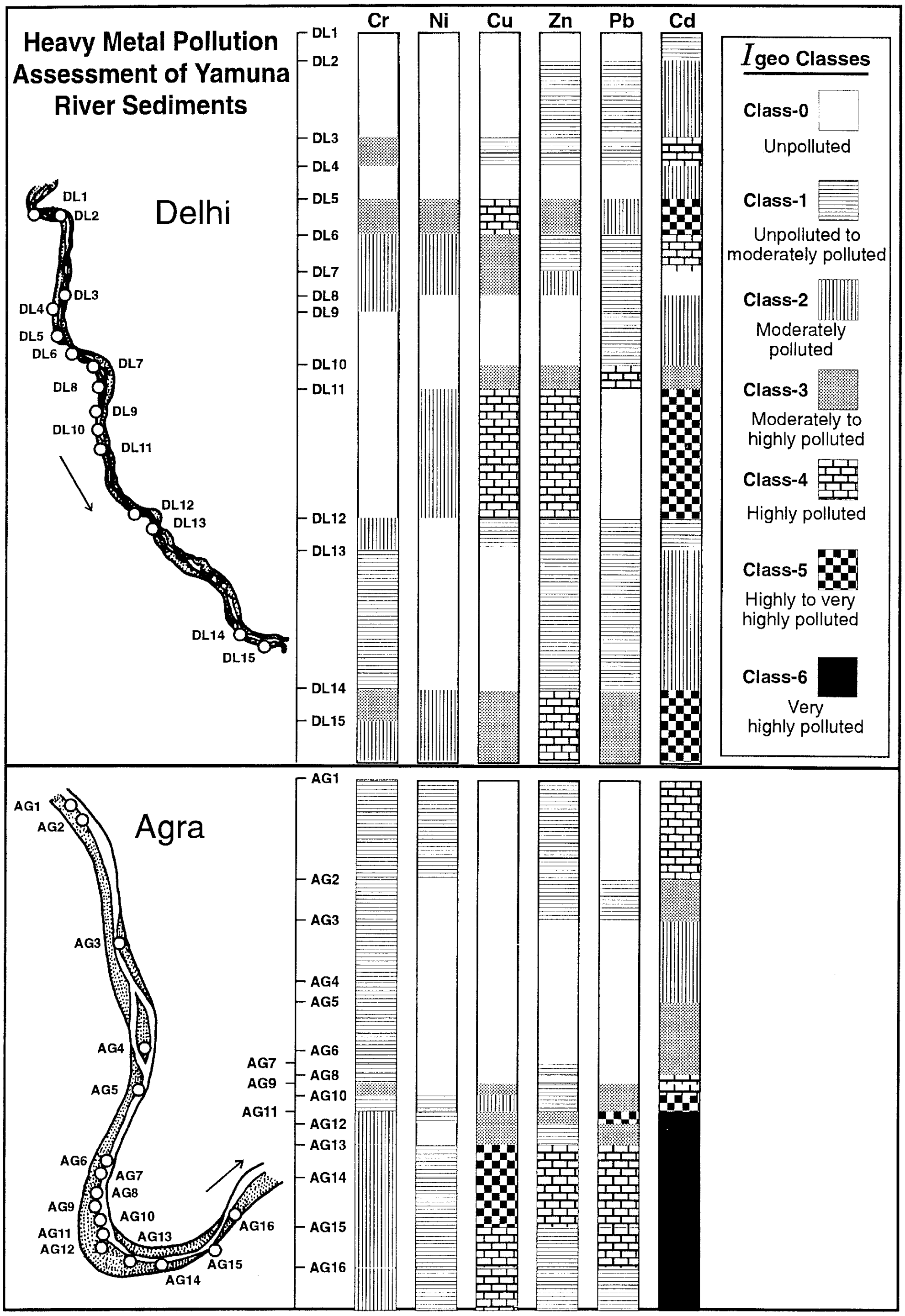

Fig. 5
Geoaccumulation index map of the Yanuna River

sources from urban centres. For the study of anthropogenic influences on the Yamuna River sediments, the average shale concentration is used as the source of the lithogenic fraction. It is estimated that 70% Cr, 74% Cu, 59% Zn, 46% Pb, 90% Cd in Delhi and 61% Cr, 23% Ni, 71% Cu, 72% Zn, 63% Pb, 94% Cd concentrations are derived from anthropogenic input in the total heavy metal concentrations (Fig. 4). These anthropogenic fractions are easily available to the river's ecobiological cycle and possibly enter into the food chain under suitable physicochemical conditions, exposing millions of people to unnaturally high metal concentrations in one or other way.

Interelement relationship

Table 3 presents the correlation matrix of heavy metals, total sediment carbon and total sediment sulfur in the river sediments. High positive correlations between Cr and Ni, Ni and C, Zn and Cu, Cd and Cu, Cu and C, Zn

Table 4
Comparision of heavy metal concentrations (in mg/kg) in Yamuna River sediments (Delhi and Agra) with Gomati River sediments (Lucknow), Ganges River sediments (Kanpur) and Neckar River sediments (Germany)

River sediments	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	Cd
Yamuna (Delhi)	394	695	40,000	18.0	159	275	561	76	4.50
(Agra)	263	718	37,700	18.7	101	339	554	168	32.50
Gomati (Lucknow)[a]	160	600	51,600	21.1	64	70	181	41	1.30
Ganges (Kanpur)[b]	214	760	42,600	18.9	52	67	189	68	1.19
Neckar (Germany)[c]	123	496	23,700	11.2	44	108	370	74	1.81

[a] Singh and others (1997)
[b] Singh (1996)
[c] Müller and others (1993)

and C, indicate their common sink in the river sediments. Total sediment carbon and sulfur contents also play an important role in controlling heavy metal concentrations in the river sediments, indicating that anthropogenic metals readily allow them to substitute in the carbonate, organic matter and sulfide phases. The negative correlation between Fe and Mn with other heavy metals indicates that hydrous oxides of Fe and Mn may provide the adsorbing sites for other heavy metals.

Quantification of sediment pollution

The geoaccumulation index proposed by Müller (1979) has been used successfully in the quantification of metal accumulation in river sediments. A geoaccumulation index map of the Delhi and Agra urban centres displays the sediment pollution levels (Fig. 5). The Yamuna River sediments are classified as unpolluted with Mn, Fe, Co; moderately polluted with Cr, Ni; highly polluted with Cu, Zn and Pb; and very highly polluted with Cd in Delhi and unpolluted with Mn, Fe, Co; moderately polluted with Cr, Ni; highly polluted with Zn and very highly polluted with Cu, Pb, Cd in Agra. Urban effluent treatment plants are being established at various locations in Agra, taking pollution control strategies of the river into consideration. This geoaccumulation index map may provide government and non-government organisations with basic information that may be useful for future environmental measures for the river and planning of city centres.

Results of this study can be combined with similar data from other geographical locations in the world. In Table 4 the average metal contents of the sediments in Delhi and Agra are compared with the average shale concentrations; the Ganges River sediments; the Gomati River sediments, a tributary of the Ganges River; and the Neckar River sediments, a tributary of the Rhine River in Germany. Concentrations of Cr, Ni, Cu, Zn, Pb and Cd metals in the Yamuna River sediments are as high as in other river sediments of India and the world.

Conclusion

The present geochemical study supports the concept that urban effluents have a great influence on the concentration and distribution of toxic heavy metals in river sediments. Urban activities are associated with the higher concentration of heavy metals such as Cr, Ni, Cu, Pb, Zn and Cd in the sediments. The basic nature of the river water, high carbonate and illite contents in the river sediments, appears to be the reason for the high heavy metal accumulation. Based on the geoaccumulation index, the Yamuna River sediments are classified as moderately to very highly polluted with Cr, Ni, Cu, Zn, Pb and Cd in Delhi and Agra. More research is needed to established the toxicological effects of these polluted river sediments on various life forms found in the environment of the river. These results can also provide base level information for future investigations dealing with the effects of urban effluent treatment plants in Agra and the bioavailability of sediment-bound heavy metals.

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