Nature of distribution of mercury in the sediments of the River Yamuna (tributary of the Ganges), India

V. Subramanian,*[a] N. Madhavan,[a] Rajinder Saxena[b] and Lars-Christer Lundin[b]

[a]*School of Environmental Sciences, Jawaharlal Nehru University, New Delhi – 110 067, India.*
E-mail: subrama42@hotmail.com; Fax: +91-11-26106501; Tel: +91-11-26704316
[b]*Department of Earth Sciences/Hydrology, Uppsala University, Uppsala, Sweden*

Received 15th November 2002, Accepted 5th March 2003
First published as an Advance Article on the web 2nd April 2003

Suspended Particulate Matter (SPM), surface (bed sediments) and short length cores of sediments collected from the largest tributary of the river Ganges, namely the river Yamuna, were analysed for total mercury as well as its fractionation in various size and chemical sites in the sediments following standard procedures. Also, attempts were made to determine the vertical distribution in sediments in relation to the recent timescale of a few decades. Our observations indicate that the SPM in general showed higher levels of total mercury compared to the surface sediments while at places the enhancement could be by a factor of 10, say around 25 μg g^{-1} in the downstream region that integrates the industrial midstream and agricultural downstream terrain near its confluence with the Ganges. Surface sediments in the upstream direction near the Himalayan foothills and SPM in the lower reaches showed significant high Index of Geoaccumulation (I_{geo}) as defined by Müller.[1] Size fractionation studies indicate that the finer fraction preferentially showed higher levels of mercury while in the lower reaches of the river, the total mercury is equitably distributed among all size fractions. The proportion of the residual fraction of mercury in relation to mobile fractions, in general decreases downstream towards its confluence with the Ganges river. In sediment cores, the vertical distribution show systematic peaks of mercury indicating that addition of this toxic metal to the aquatic system is in direct proportion to the increase in various types of human activities such as thermal power plants, land use changes (urbanisation) in the midstream region and intensive fertiliser application in lower reaches of this vast river basin.

Introduction

Mercury and its compounds have caused a variety of documented, significant global adverse impacts on human health and the environment throughout the world.[2–11] Even areas with minimal local and national mercury releases, such as in the Arctic, are adversely affected due to the transcontinental and global transport of mercury.[12,13] Studies from the Ganges estuary (Sagar Island) indicate that organisms of bivalves show 0.06–2.24 mg total Hg kg^{-1} dry wt.[14] Some effects of mercury are linked to long-range transport which occurs where mercury is released into the air which then comes into contact with humans and wildlife.[15] The Indian submission on global mercury assessment reports observed elevated mercury exposure in an area influenced heavily by emissions from thermal power plants.[16] Elevated levels of Hg in air may also occur downwind from some types of emissions sources such as chlor-alkali plants which are still active in India.[16] There have been major changes in emissions in 1995 compared to 1990, with respect to the location of major emission regions contributing the most to the global emission survey of the element. Whereas the mercury emissions in Europe and North America have decreased quite substantially during the period from 1990 through 1995, emissions in Asia, particularly in China and India, have increased significantly.[16] The Asian sources contributed about 30 percent to the total emissions of mercury in 1990, compared to 56 percent in 1995. An increase of more than 250 metric tonnes were estimated for China between the years 1990 and 1995. The increase of mercury emissions in China from 1990 through 1995 is clearly related to the increase of coal combustion in the country.[16] The mercury emission increase due to the increased combustion of coal has overcome a slight reduction of emission of air pollutants in the country due to the installation of high efficient emission control devices starting in the mid-1990's. So, atmospheric mercury can be deposited to aquatic ecosystems through both wet (rain or snow) and dry (vapour adsorption and particulate deposition) processes over the Himalayas which may be the source of Hg in the river water/sediment head water system. Elevated mercury levels also have been measured in numerous freshwater fish species (0.069–3.920 mg kg^{-1} wet wt), sediment (0.16–5.71 mg kg^{-1}) and water (0.17–2.351 mg L^{-1}) throughout the Indus River.[17] Since the sediment load of rivers such as the Ganges and the Brahmaputra is known to be very large, about a billion tonnes per year,[18] it will be interesting to find out about the distribution and fractionation behaviour of this toxic element in the high pressure environment with a combined population of over 300 million people thereby reflecting pressure on various types of land use in the entire region. With this objective, the present work was undertaken in the Yamuna river, a major tributary of the Ganges with the Himalayan watershed in the upstream region, and also housing a large thermal power/industrial base in the midstream region and very diverse and intensive agricultural activity in the lower reaches of the river basin.

Methodology

The Yamuna river originates from the glacier region of the Himalayas at an elevation of about 6320 m and covers a catchment area of about 0.3 million km^2 with an annual discharge of 131.7 km^3. Tertiary age sedimentary rocks of various lithological units constitute the geological framework in the upper reaches while the remaining 60% of the basin area is predominantly alluvial terrain of tertiary to quaternary age.[19] All along its 1400 km length, the river is joined by many tributaries draining a variety of geologies and land and soil

DOI: 10.1039/b211263a

types including forested areas, basaltic lithology and red soils. The river finally merges with the mighty Ganges at Naini after it passes through a number of urban regions such as Wazirabad, Mathura and Agra. Based on land use pattern, the river is divided into three sectors. The upper reaches represent catchment and low population density, the mid-stream reflect intensive urban and industrial activity while the lower reaches after Agra primarily reflect various levels of agricultural activities.

Surface (Bed Sediments) and core sediments were collected from different locations as mentioned in Fig. 1, at low flow summer time (April–May 1995), whereas suspended Particulate Matter (SPM) were collected during high flow monsoon time (October 1995). Samples of bed sediment samples were collected from the top 5 cm of the sediment. Core sediment was collected in a pre washed (1 M HNO_3) 5 cm width and 100 cm length polycarbonate tube pivoted to ensure a vertical position. All sediment samples were preserved at 4 °C until laboratory processing. Surface water was collected in the field with the help of a wide mouth mug and transformed into a five litre jerrycan. SPM was allowed to settle and the clear water was siphoned off. Then it has been transformed into a 500 ml glass bottle, brought to the laboratory, filtered and digested for metal analysis. The amount of SPM was determined by filtering a known aliquot of water (usually 250 ml) through a tared 0.45 μm, 47 mm (diameter) polycarbonate filter. SPM size was determined by Fritsch Laser Particle Sizer. Bed sediment bulk samples were size-fractionated as sand and silt through a Fritish sieve shaker and classified, whereas wet sieving was used for <63 μm size samples. Total Organic Carbon (TOC) was estimated from the difference between total carbon and inorganic carbon through an Eltra carbon analyser for bed sediments, selected core sediments and SPM. Prior to inorganic carbon analysis, the samples were treated with H_2O_2 to remove organic carbon. We followed the method of Loring and Rantala[20] and Allen *et al.*,[21] for Hg sample preparation. It consists of oxidizing the sediment sample (1 g dry weight) by digesting it with a mixture of concentrated nitric acid and sulfuric acid at 60 °C for 1 h and reducing Hg to its elemental state with stannous chloride. The mercury vapor is then passed through a quartz absorption cell of an AAS where its concentration was measured at 253.7 nm; slit 0.7 nm and absorption were noted down. The Hg was measured with reference to United States Geological Survey (USGS) and Canadian Certified Reference Materials Project (CCRMP) standard soil materials. They are as follows GXR-2 (2.64 ± 0.082); GXR-5 (0.15 ± 0.003); GXR-6 (0.06 ± 0.001); SO-1 (0.018 ± 0.002); SO-2 (0.076 ± 0.005); SO-3 (0.016 ± 0.001) & SO-4 (0.028 ± 0.003). The data in parenthesis are observed values (μg g^{-1}) and standard deviations for Hg in our data fall within 10% of certified values. The detection limit for Hg on AAS was 10 μg L^{-1}.

Results and discussion

The mercury levels at various locations show from 0.01 to 25.2 μg g^{-1} in SPM and 0.01 to 2.6 μg g^{-1} in surface sediments and are generally above the uncontaminated aquatic clay and shale values as indicated by Salomons and Förstner.[22] The downstream region, representing the combined effect of diverse lithology, land use and soil conditions at all upper locations, show higher values compared to the data near the catchment region. Among the three tributaries of Yamuna, Ken brings a low sediment load but high Hg load, but their high values are diluted by high sediment load with low Hg being brought from the upstream direction. So the downstream of Ken, in the Yamuna the Hg level in the SPM marginally increases. SPM towards the confluence with the Ganges, near Allahabad, show mercury levels higher than the world average values[23] (0.2 μg g^{-1}) and also higher compared to the surface or bed sediments representing size control on the mercury levels in river-borne sediments. Among the three main tributaries,

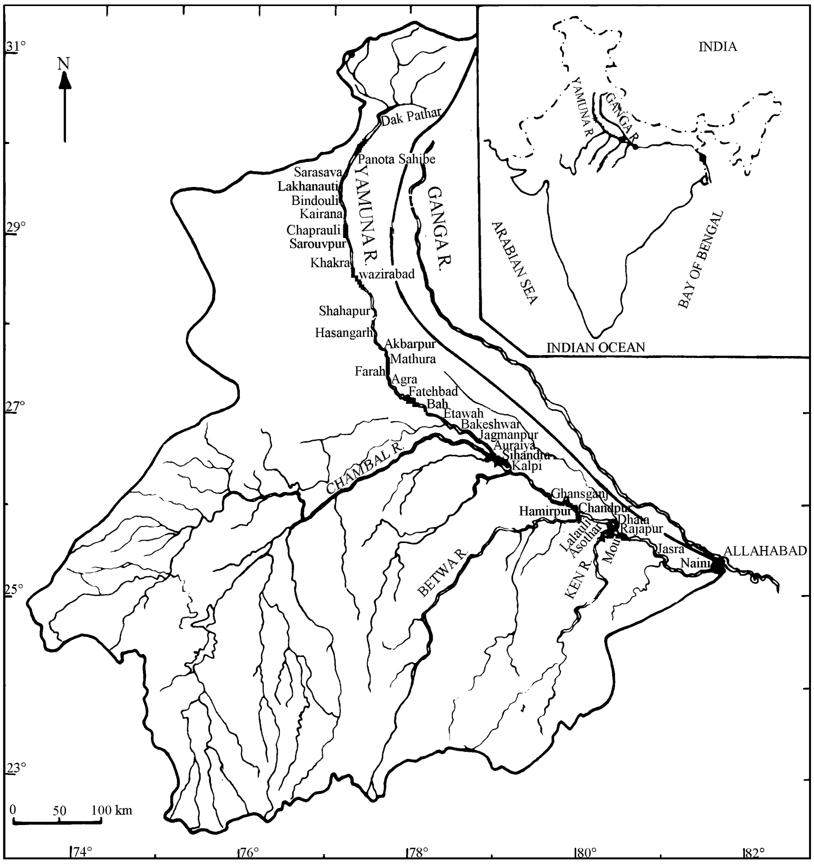

Fig. 1 Map showing sampling locations.

Table 1 List of locations and results of the Suspended Particulate Matter (SPM) and Bed Sediment mercury (Hg) with reference to organic carbon (C-org) concentration. Data on chemical fractionation of Hg is for bed sediments

Location	Distance/ km	SPM/ mg L^{-1}	Mean size (SPM)/μm	Hg (SPM)/ μg g^{-1}	C-org (SPM, %)	I_{geo} (SPM)	Hg (Bed)/ μg g^{-1}	C-org (Bed, %)	I_{geo} (Bed)	Exchangeable (Hg)/μg g^{-1}	Carbonate (Hg)/μg g^{-1}	Iron (Hg)/ μg g^{-1}	Organic (Hg)/ μg g^{-1}	Residual (Hg)/ μg g^{-1}
Dak Pathar	80	60	—	0.37	1.26	0.3	0.19	0.46	−0.7	0.10	0.06	0.04	0.7	61.6
Panota Sahibe	200	30	—	0.01	0.84	−5.4	0.46	0.33	0.6	0.36	0.04	0.08	0.6	104.6
Sarsava	260	460	11.73	0.15	0.61	−1.0	2.59	0.45	3.1	0.08	0.02	0.19	0.8	61.6
Lakhanauti	300	10	—	0.29	0.45	0.0	2.13	0.48	2.8	0.06	0.02	0.15	0.5	76.2
Bindouli	330	40	—	0.22	0.36	−0.4	1.76	0.81	2.6	0.04	0.06	0.06	0.5	7.3
Kairana	370	60	—	0.15	0.49	−1.0	0.28	1.05	−0.1	0.08	0.13	0.04	0.5	4.6
Chaprauli	410	110	—	1.11	0.73	1.9	0.19	0.55	−0.7	0.04	0.02	0.08	0.3	4.0
Sarouvpur	440	130	—	0.62	0.42	1.1	0.09	0.82	−1.7	0.08	0.13	0.19	0.5	4.6
Khakra	490	110	3.83	0.21	0.38	−0.5	0.19	0.74	−0.7	0.06	0.04	0.29	0.3	4.0
Wazirabad (Delhi)	540	140	8.7	0.21	1.23	−0.5	0.37	0.17	0.3	—	—	—	—	—
Shahapur	650	100	11.33	0.42	0.31	0.5	0.56	0.42	0.9	—	—	—	—	—
Hasangarh	690	130	10.84	0.83	—	1.5	1.30	0.42	2.1	—	—	—	—	—
Akbarpur	760	320	9.76	0.48	0.24	0.7	0.83	0.50	1.5	0.01	0.31	0.34	0.7	95.4
Mathura	800	390	9	0.48	0.31	0.7	0.83	0.63	1.5	0.06	0.04	0.15	0.5	11.3
Farah	830	590	9.13	0.55	0.48	0.9	0.65	0.95	1.1	0.10	0.04	0.65	0.5	3.3
Agra	900	460	6.86	0.42	0.35	0.5	0.28	0.43	−0.1	0.02	0.15	0.27	0.6	3.3
Fatehbad	950	600	6.07	0.42	0.22	0.5	0.01	0.37	−5.1	0.13	0.19	0.27	0.4	1.3
Bah	980	800	6.97	0.35	0.31	0.2	0.09	0.50	−1.7	0.10	0.17	0.38	0.6	2.0
Etawah	1020	470	3.88	0.28	0.30	−0.1	0.19	1.34	−0.7	0.15	0.02	0.48	0.5	2.6
Bakeswar	1070	350	3.26	0.69	0.23	1.2	0.83	1.24	1.5	0.10	0.13	0.25	0.5	2.6
Jagmanpur (T. Champal)	1100	520	2.05	1.94	1.45	2.7	0.74	—	1.3	0.32	0.08	0.38	0.9	0.03
Auraiya	1140	3060	28.43	0.01	1.28	−5.4	0.37	—	0.3	0.34	0.06	0.28	0.7	0.3
Sihandra	1155	980	2.28	0.90	—	1.6	0.65	—	1.1	—	—	—	—	—
Kalpi	1170	1170	3.4	2.56	1.15	3.1	1.20	—	2.0	0.36	0.02	0.28	0.8	0.1
Ghansganj	1180	730	4.16	0.21	0.70	−0.5	1.02	—	1.8	0.38	0.04	0.52	0.7	0.1
Hamirpur (T. Betwa)	1185	280	3.91	0.42	0.38	0.5	0.83	0.86	1.5	0.44	0.22	0.48	0.7	0.2
Chandpur	1190	800	4.07	16.84	0.69	5.8	1.57	—	2.4	0.32	0.28	0.45	0.8	0.1
Lalauli (T. Ken)	1200	620	1.77	25.22	0.63	6.4	1.11	0.62	1.9	0.32	0.24	0.53	0.7	0.1
Kisanpur	1210	820	4.97	0.01	0.82	−5.4	0.83	—	1.5	0.38	0.40	0.52	0.7	0.01
Asothar	1230	170	1.82	1.39	—	2.2	0.93	—	1.6	0.32	0.26	0.50	0.7	0.1
Dhata	1255	670	1.73	0.83	1.29	1.5	1.11	—	1.9	0.40	0.30	0.43	0.7	0.1
Rajapur	1290	770	2.23	0.76	0.71	1.3	0.93	—	1.6	0.30	0.30	0.43	0.6	0.1
Mou	1340	470	36.51	1.39	1.19	2.2	1.48	—	2.3	0.32	0.24	0.33	0.7	0.03
Jasra	1370	590	2.16	0.35	0.99	0.2	0.65	—	1.1	0.26	0.42	0.41	0.7	0.01
Naini (Allahabad)[a]	1400	360	1.75	2.56	0.17	3.1	1.11	0.87	1.9	0.36	0.36	0.01	0.6	0.1
Mean	—	496.29	—	1.82	0.66	0.57	0.81	0.65	0.88	0.21	0.15	0.31	0.60	14.56
Min	—	10.00	—	0.01	0.17	−5.42	0.01	0.17	−5.06	0.01	0.02	0.01	0.28	0.01
Max	—	3060.00	—	25.22	1.45	6.39	2.59	1.34	3.11	0.44	0.42	0.65	0.87	104.64
SD	—	539.25	—	4.95	0.38	2.47	0.60	0.30	1.60	0.14	0.13	0.17	0.15	30.08
RSQ (with distance)	—	0.243	0.012	0.066	0.016	—	0.001	0.127	—	0.436	0.386	0.403	0.188	0.392
RSQ (with Hg in SPM)	—	0.008	0.031	—	0.001	—	0.048	0.000	—	0.062	0.051	0.079	0.067	0.026
RSQ (with Hg in bed)	—	—	—	—	—	—	—	0.005	—	0.026	0.002	0.000	0.133	0.048

[a] Confluence point for R. Yamuna and R. Ganges.

namely Ken, Betwa and Chambal, the SPM of Ken contributes a significant load of mercury to the Yamuna, as indicated by their location in the Table 1.

The extent of pollution in an aquatic system can be determined by means of the heavy metal load in sediments, the pre-civilizational level, by subtracting it from existing values for metal concentrations in order to derive the total enrichment caused by anthropogenic influences. It has been introduced by Muller, as indicated by Salomons and Förstner.[22] which is called 'index of geoaccumulation':

$$I_{\text{geo}} = \log_2 C_n/1.5\ \text{B}_n$$

whereas C_n is the measured concentration of the element 'n' in the pelitic sediment fraction (< 2 μm) and B_n is the geochemical background value in fossile argillaceous sediment. Since short dated sedimentary cores, which provide a recent historical record of events occurring in the watershed of the Yamuna

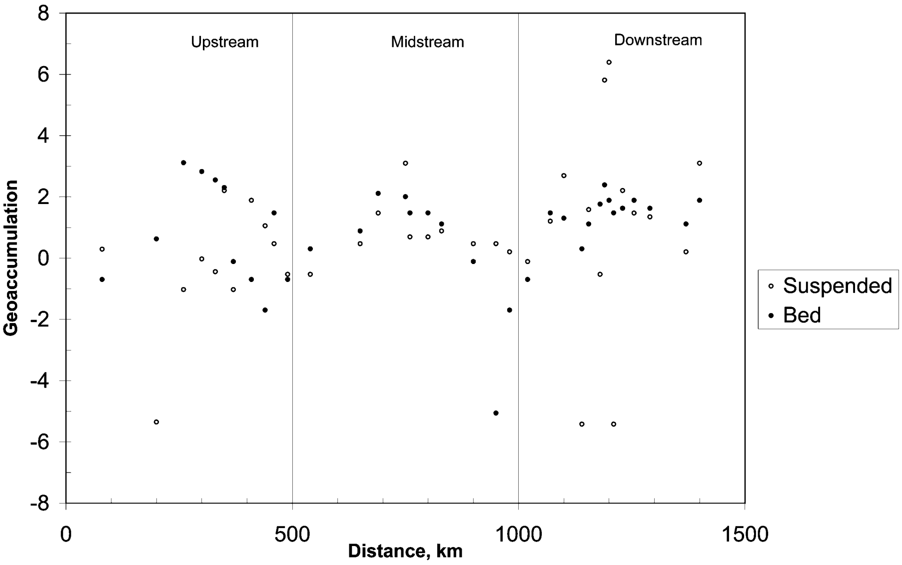

Fig. 2 Geoaccumulation index of Yamuna River sediments for Hg at different locations.

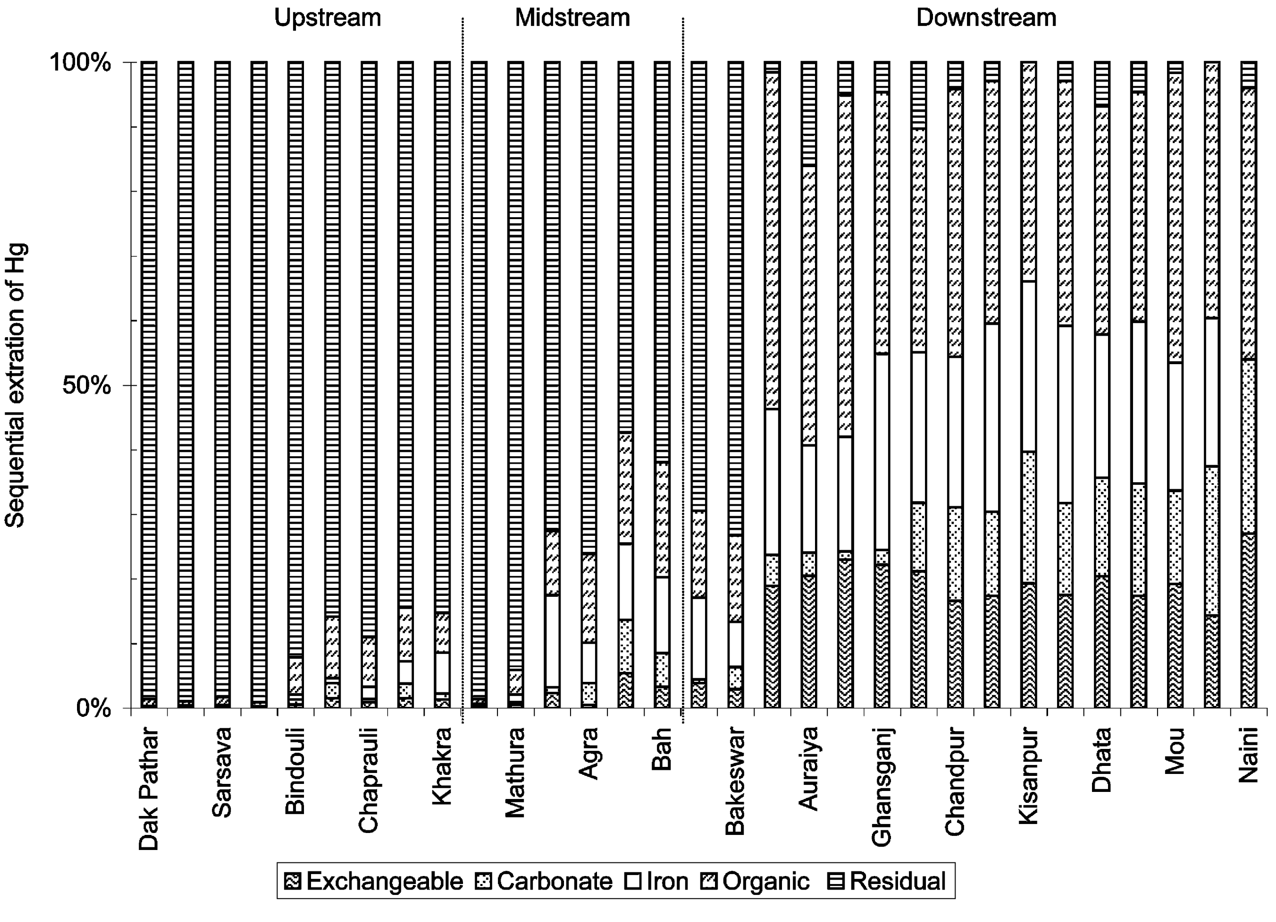

Fig. 3 Variation in the chemical fractionation behaviour of Hg in the downstream direction for the River Yamuna. Last point in this direction represents the junction with the River Ganges.

River,[24] these would enable an estimation of both the background levels and the changes in input of an element over an extended period of time. Background levels may be regarded as the levels that exist on top of which anthropogenic materials have been added.[25] The other wide range of techniques[25] used to normalise the environmental data is the mobilization factor (MF) where MF = antropogenic emission rate/natural emission rate. Alternatively, enrichment factor (EF) may be also considered, EF = {(m)air/(m)Crust}/{(Al)crust/(Al)air}. But each such factor addresses specific questions and $I_{\rm geo}$ reflects an integrated number. Following the procedures of Salomons and Förstner[22] and using a background value of 0.2 μg g^{-1} for mercury levels in aquatic shale and clays, $I_{\rm geo}$ reflecting secondary enrichment in the modern aquatic environment, was calculated for various locations in the Yamuna river system and Fig. 2 shows the trends in the $I_{\rm geo}$ values at different location in the flow direction of the river. Except for a few locations, the SPM and the surface sediments consistently show enhanced numbers of $I_{\rm geo}$; even in the upper reaches, the values are higher due to handling of explosives near the river banks by the Military services while in the mid and lower reaches, either industrial/thermal power or fertiliser run-off contribute the added mercury. Thus additional mercury contribution comes from all parts of the river basin. Because there are intensive re-suspension mechanisms operating in such large sediment load rivers as the Yamuna, there is no differentiation in $I_{\rm geo}$ values for the surface and SPM in the river system.

The sequential extraction of sediments, as shown in Table 1 and Fig. 3 suggests that towards the downstream direction, the toxic metal Hg increasingly gets associated with various mobile fractions such as the exchange, organic and the easily reducible phases. The sequential extraction results indicate that forms associated with the exchangeable, carbonate, reducible and residual fraction play a significant role in the chemical mobilisation of mercury in these sediments with relation to distance ($r^2 \geqslant 0.4$) from the source of origin (Fig. 4). Organic bound Hg remained constant or increased slightly in the downstream direction through the study area, whereas the residual Hg decreased significantly downstream especially in the reach of the midstream (Fig. 4). In upstream the Hg was mostly concentrated in the residual fraction, although it was also present in other fractions. In midstream and downstream exchangeable, carbonate and easily reducible phases Hg is present at all the stations in this river, but at higher levels while comparing to upstream. The maximum variability was observed in the Hg fraction bound to organic fraction, ranging from 0.28 to 0.87 μg g^{-1}. Exchangeable Hg predominates in the downstream (0.15 μg g^{-1}) and gradually increased in content with increasing distance (0.44 μg g^{-1}). At the confluence of tributary River Ken with River Yamuna, Hg distribution is dominated by the organic-bound fraction (0.53 μg g^{-1}). At all these locations, the reducible and organic-bound Hg fractions are comparatively low in upstream.

Thus variations in the levels of mercury either as a function of size, as was shown in Fig. 5, or the bulk total mercury in SPM or surface sediments at different locations as was shown in Table 1 may simply reflect changing partitioning behavior of the toxic metal in different mobile fractions in response to local aquatic variables such as pH, Eh and other water quality parameters or disturbance in the sediment column (very common in any large river systems such as the Ganges basin) due to re-suspension, burrowing organisms *etc.*

By using precise grain size separation the relative distribution of mercury among all size populations of the river sediments was carried out. It indicates equitable fractionation of mercury within the sediments and is shown in Fig. 5. Since the clay content was very low, it could not be separately fractionated and it may explain the lack of preferential sediment size for mercury dispersal.

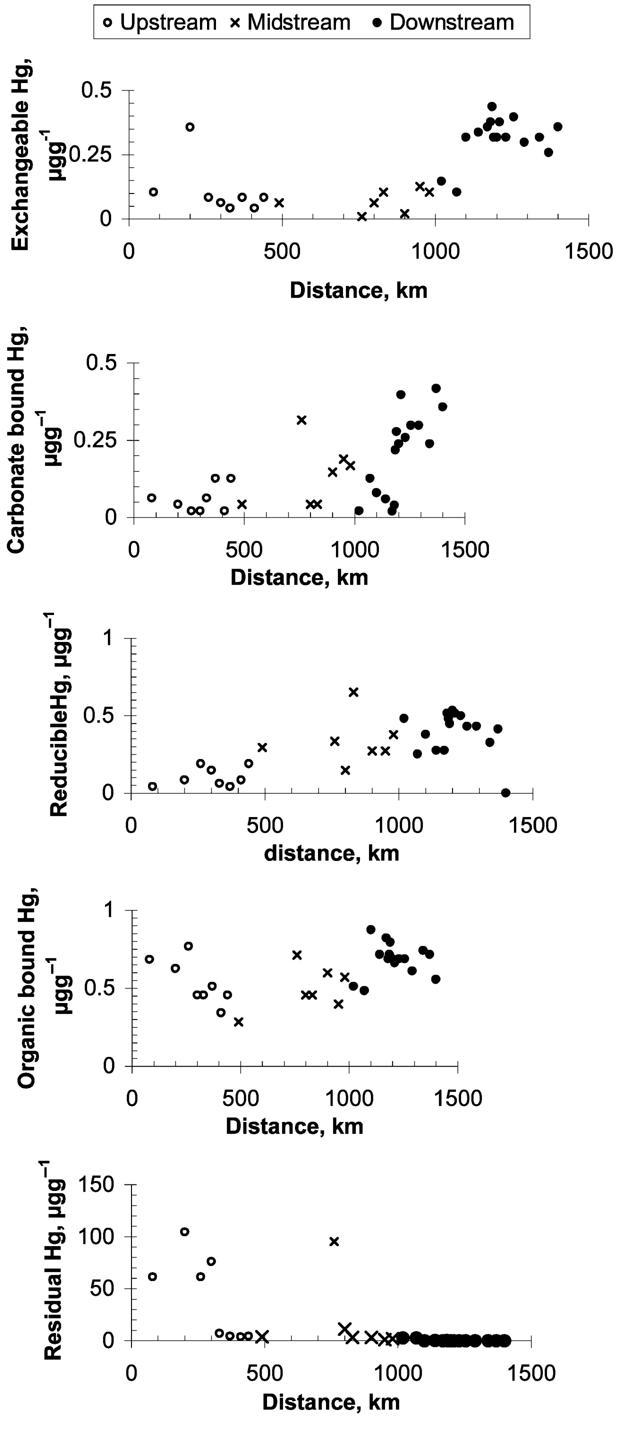

Fig. 4 Relationship between distance *versus* chemical fractionation behaviour of Hg for the River Yamuna.

The percentage distribution of sand, silt and clay in the sediments of Yamuna River is shown in Table 2. The differences in grain size content of sediments collected at increasing distances from the confluence point (Naini) for River Yamuna and River Ganges was found to be significant ($r^2 = 0.9$ for sand and 0.8 for silt), but it was not significant for Hg content in any size fraction at different locations in flow direction ($r^2 = 0.4$). The vertical distribution of mercury in different sediment cores at selected locations representing all the regions of the river basin is illustrated in Table 3 and in Fig. 6. One can see that there are several peaks at different and frequent depth intervals where mercury concentration shows maximum levels though the values in each such peak may vary from depth to depth and from location to location. The regression of the Hg with TOC concentration was tested and

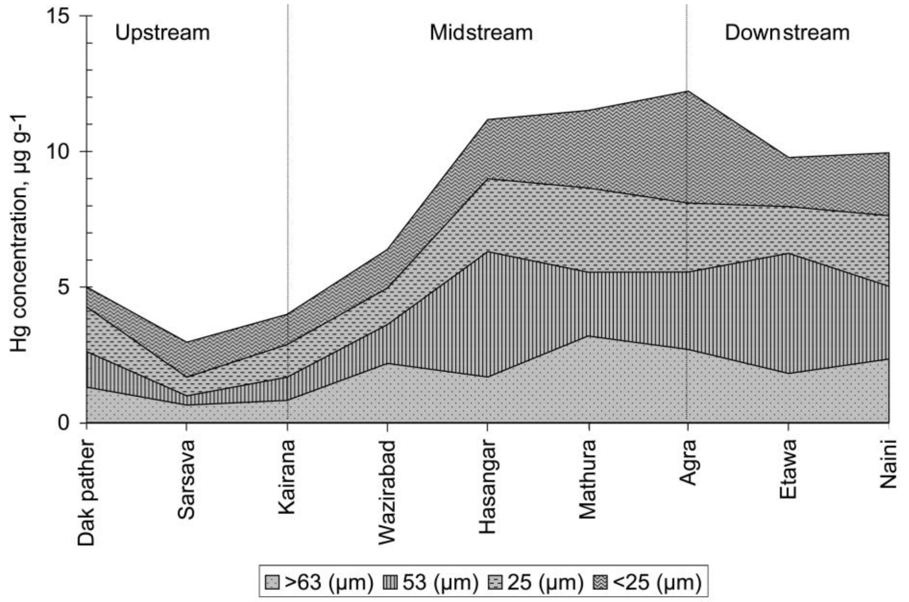

Fig. 5 Mercury in various size fractions of the Yamuna River bed sediments in the downstream direction. Size fractionation done by conventional wet sieving method. Size range expressed in µm.

Table 2 Mercury in various size fractions (µm) and their concentrations in µg g^{-1}

Location	Distance/km	Sand (%)	Silt (%)	Clay (%)	>63/µm	63–53/µm	53–25/µm	<25/µm
Dak pather	80	11	80	10	1.3	1.3	1.7	0.7
Sarsava	260	14	84	2	0.6	0.3	0.7	1.3
Kairana	370	13	71	16	0.8	0.9	1.2	1.1
Wazirabad	540	18	73	9	2.2	1.4	1.3	1.4
Hasangar	690	23	72	6	1.7	4.6	2.7	2.2
Mathura	800	38	62	0.01	3.2	2.4	3.1	2.9
Agra	900	58	33	10	2.7	2.9	2.5	4.1
Etawa	1020	42	54	5	1.8	4.4	1.7	1.8
Naini	1400	67	33	0.01	2.3	2.7	2.6	2.3
RSQ (with distance)		0.9	0.8	0.2	0.4	0.4	0.4	0.4
RSQ (with Sand %)		—	—	—	0.5	0.2	0.4	0.6
RSQ (with Silt %)		—	—	—	0.4	0.2	0.3	0.6
RSQ (with Clay %)		—	—	—	0.1	0.1	0.1	0.1

Table 3 Core profile of Hg concentration (µg g^{-1}) in the River Yamuna

Depth/cm	Dak Pathar	Sarsava	Shahapur	Mathura	Agra	Etawah	Jagmanpur	Hamirpur	Lalauli	Rajapur	Naini
2.5	3.2	0.9	2.5	1.4	0.8	0.1	0.2	0.7	0.5	0.9	0.6
7.5	2.4	1.1	1.6	1.4	1.5	0.4	0.1	0.9	0.6	0.9	1.1
12.5	1.3	0.9	1.7	0.9	1.7	0.2	0.2	1.1	0.4	1.2	0.8
17.5	1.4	0.6	1.8	1.6	0.9	0.1	0.3	1.0	0.6	1.1	1.9
22.5	2.4	2.4	2.4	1.5	0.4	0.2	0.5	1.8	0.6	0.9	1.3
27.5	2.8	1.0	1.6	1.1	0.6	0.4	0.6	1.5	0.5	0.5	1.4
32.5	3.5	1.9	1.9	1.5	0.2	0.6	0.6	1.4	0.5	0.6	1.2
37.5	2.0	1.1	1.5	1.1	0.1	0.9	0.6	1.2	0.9	0.5	1.4
42.5	1.7	1.2	1.4	1.4	0.1	0.5	0.6	1.4	0.6	0.4	1.1
47.5	1.1	0.4	1.6	0.9	0.4	0.6	0.6	1.9	1.0	0.2	1.5
52.5	4.4	0.2	2.0	0.8	0.6	0.3	0.2	1.9	0.8	0.2	1.1
57.5	1.0	0.3	1.6	0.6		2.0	0.2	1.7	0.9	0.3	1.2
62.5	1.1	0.5	1.6	4.1		0.3	0.4	2.0	0.7	0.3	1.3
67.5	1.3	0.3	2.0	0.2		1.3	1.3	2.0	1.0	0.2	2.3
72.5	1.6	0.3		1.5		0.4	0.9	2.0			1.5
77.5	4.8	0.5		1.3			0.7	0.8			1.6
82.5	1.7			1.0			1.0	1.0			1.2
87.0	0.7						1.1	1.1			
92.0								5.5			
Mean	2.1	0.9	1.8	1.3	0.7	0.5	0.6	1.6	0.7	0.6	1.3
Min.	0.7	0.2	1.4	0.2	0.1	0.1	0.1	0.7	0.4	0.2	0.6
Max.	4.8	2.4	2.5	4.1	1.7	2.0	1.3	5.5	1.0	1.2	2.3
RSQ with depth	0.020	0.314	0.092	0.000	0.493	0.243	0.515	0.223	0.542	0.822	0.183

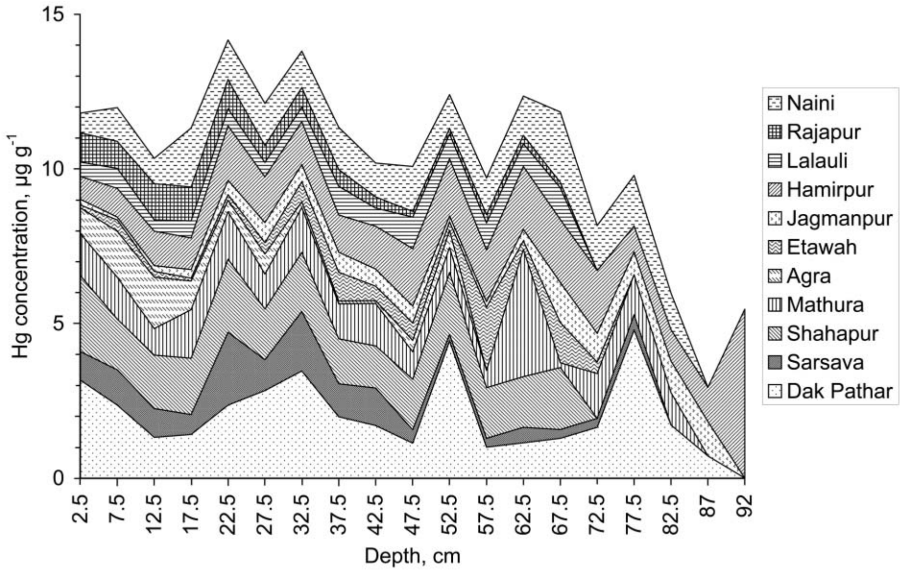

Fig. 6 Vertical depth profile of Hg concentration of sediment cores at selected locations in the River Yamuna.

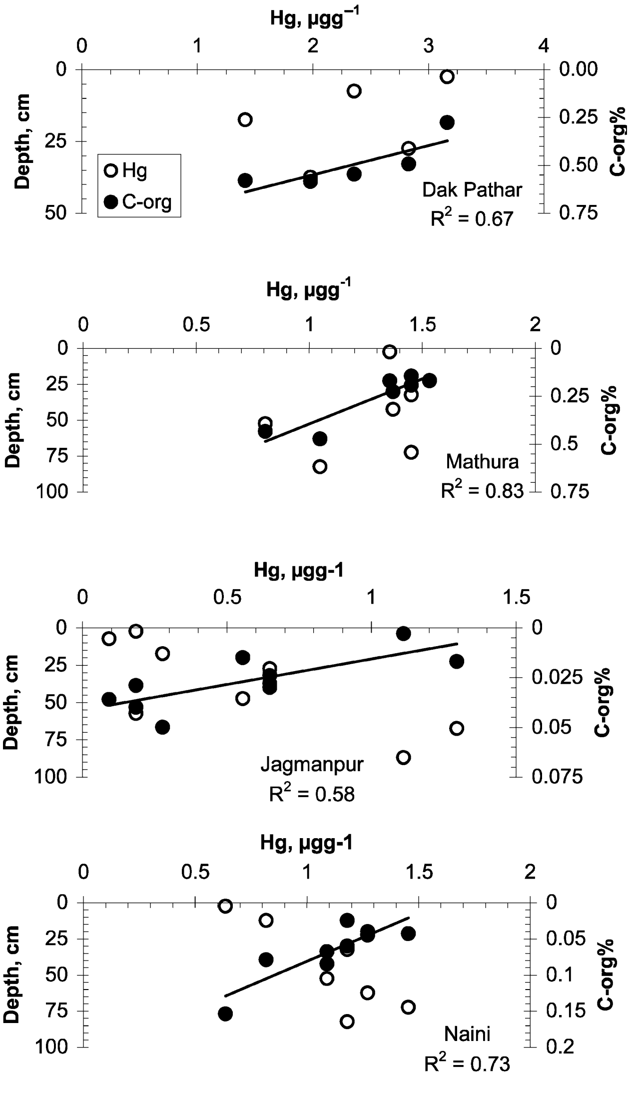

Fig. 7 Variations in the levels of mercury and organic carbon at different depth intervals for the river Yamuna. Regression line for the relation between mercury and organic carbon.

the significant results ($P < 0.001$) are given in Fig. 7. Decreasing TOC concentrations may be caused by natural changes in climate or sedimentation rate. Therefore normalisation of Hg with TOC or clay content vary spatially.[26] Due to variable rates in sediment accumulation at different time intervals and locations, mercury deposition with the river sediment varies widely at different timescales within the last half-century considered in this study. This time interval also represents the intensive agricultural and industrial activity in this river basin, considered one of the most densely populated regions in the Indian sub-continent. Since ^{137}Cs was also used in the determination of sedimentation rates[24] that works out to be in the range 2–4 cm per year, the upper time interval is 1993. The present day mercury levels as shown in Table 1 in combination with Table 3 clearly suggests that the supply of mercury to the river system *via* the sediment and soil erosion has been significantly increasing in recent times.

Conclusion

The tributary Ken shows the maximum amount of Hg in SPM (25 µg g^{-1}). In the entire river basin, SPM generally shows higher levels of Hg compared to bed sediments. A significant amount of Hg was found to be associated with the non-residual mobile fractions in the bed sediments, indicating that this metal is potentially bio-available. Further, Hg in the immobile or residual fraction decreases in the flow direction. Hg concentration in any size fraction was not correlated well ($r^2 = 0.4$) with distance all along the flow direction from the catchment to the point of confluence with the River Ganges. In sediment cores the Hg concentration and the TOC show good correlation ($r^2 = 0.67$ to 0.83 at different locations). At three locations, near the confluence points with the tributaries Ken and Chambal, the vertical distribution of Hg shows good correlation with depth.

The sediments of the Yamuna river supply significant levels of the toxic metal mercury in mobile fractions and there are indications that the transport and deposition of this metal has been increasing in the downstream direction particularly in the last fifty years. While there are no size preferential sites for mercury due to paucity of very fine clay fractions in these sediments, the proportion of various mobile fractions show a definite increasing trend over its 1400 km stretch in the downstream direction towards the confluence with the river Ganges and hence this metal gets into the larger river system with high amounts of mobile components and eventually these are delivered along with the very large annual sediment load of about 400 million tonnes, a further 1000 km in the downstream direction to the Bay of Bengal.[18] Thus, our study has tried to understand the transportation, deposition and fractionation of Hg in the sediments of a large river basin draining one of the densely populated regions of the world.

Acknowledgements

The authors would like to thank Prof. Martin J. Haigh, Oxford Brookes University, Oxford for language editing and two anonymous reviewers for valuble discussions and constructive comments on the manuscript.

References

1 G. Müller, *Umschau*, 1979, **79**, 778–783.
2 T. R. Moore, J. L. Bubier, A. Heyes and R. J. Flett, *J. Environ. Qual.*, 1995, **24**, 845–850.
3 R. Crompton, in *Toxicants in the Aqueous Ecosystem*, John Wiley & Sons, Chichester, 1997, pp.185–218.
4 C. L. Babiarz, J. P. Hurley, J. M. Benoit, M. M. Shafer, A. W. Andren and D. A. Webb, *Biogeochemistry*, 1998, **41**, 237–257.
5 B. J. Harland, D. Taylor and A. Wither, *Sci. Total Environ.*, 2000, **253**, 45–62.
6 R. C. R. Martin-Doimeadios, J. C. Wasserman, L. F. G. Bermejo, D. Amouroux, J. J. B. Nevado and O. F. X. Donard, *J. Environ. Monit.*, 2000, **2**, 360–366.
7 D. A. Roth, H. E. Taylor, J. Domagalski, P. Dileanis, D. B. Peart, R. C. Antweiler and C. N. Alpers, *Arch. Environ. Contam. Toxicol.*, 2001, **40**, 161–172.
8 D. Fabbri, G. Gabbianelli, C. Locatelli, D. Lubrano, C. Trombini and I. Vassura, *Water, Air, Soil Pollut.*, 2001, **129**, 143–153.
9 A. Helland, *Water, Air, Soil Pollut.*, 2001, **126**, 339–361.
10 B. S. Leady and J. F. Gottgens, *Wetlands Ecology and Management*, 2001, **9**, 349–361.
11 A. Kishe and J. F. Machiwa, *Environ. Int.*, 2003, **28**, 619–625.
12 G. Asmund and S. P. Nilsen, *Sci. Total Environ.*, 2000, **245**, 61–72.
13 S. C. Jewett, X. Zhang, A. S. Naidu, J. J. Kelley, D. Dasher and L. K. Duffy, *Chemosphere*, 2003, **50**, 83–392.
14 B. Bhattacharya and S. K. Sarkar, *Chemosphere*, 1996, **33**, 147–158.
15 D. T. Waite, A. D. Snihura, Y. Liu and G. H. Huang, *Chemosphere*, 2002, **49**, 341–351.
16 UNEP, Report of the Global Mercury Assessment Working Group on the Work of its First Meeting, Geneva, Switzerland, 9–13 September 2002. Website: www.chem.unep.ch.
17 J. Tariq, M. Ashraf, M. Jaffar and M. Afzal, *Water Res.*, 1996, **30**, 1337–1344.
18 V. Subramanian, in *A Text Book in Environmental Science*, Narosa Publishing House, New Delhi, 2002, pp.43–72.
19 P. K. Jha, V. Subramanian, R. Sitasawad and R. Van Greiken, *Sci. Total Environ.*, 1990, **95**, 7–27.
20 D. H. Loring and R. T. T. Rantala, *Earth Sci. Rev.*, 1992, **32**, 235–283.
21 S. E. Allen, J. A. Parkinson and A. P. Rowland, in *Pollutants in Chemical Analysis of Ecological Materials*, ed. S. E. Allen, Blackwell Scientific Publ., Oxford, 1989, pp. 201–239.
22 W. Salomons and U. Förstner, in *Metals in the Hydrocycle*, Springer-Verlag, Berlin, Heidelberg, 1984, pp. 79–81.
23 K. K. Turekian and K. H. Wedepohl, *Bull. Geol. Soc. Am.*, 1961, **72**, 175–192.
24 D. P. Saxena, P. Joos, R. Van Grieken and V. Subramanian, *J. Radioanal. Nucl. Chem.*, 2001, **251**, 399–408.
25 E. Fergusson, in *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, Oxford, 1990, pp. 143–199.
26 K. Brack and R. L. Stevens, *Environ. Geol.*, 2001, **40**, 1017–1029.