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Geochemistry and magnetic measurements of suspended sediment in urban sewage water vis-à-vis quantification of heavy metal pollution in Ganga and Yamuna Rivers, India

Munmun Chakarvorty · Akhil Kumar Dwivedi · Anil Dutt Shukla · Sujeet Kumar · Ambalika Niyogi · Mavera Usmani · Jayanta Kumar Pati

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Abstract Sewage water is becoming a key source of heavy metal toxicity in large river systems worldwide and the two major Himalayan Rivers in India (Ganga and Yamuna) are severely affected. The high population density in the river banks combined with increased anthropogenic and industrial activities is contributing to the heavy metal pollution in these rivers. Geochemical data shows a significant increase in the concentration of all heavy metals (Pb, 48–86 ppm; Zn, 360–834 ppm; V, 45–101 ppm; Ni, 20–143 ppm; Cr, 79–266 ppm; Co, 8.62–22.12 ppm and Mn, 313–603 ppm) in sewage and mixed water (sewage and river water confluence site) samples due to increased effluent discharge from the catchment area. The ΣREE content of sewage water (129 ppm) is lower than the average mixed water samples (142 ppm). However, all the samples show similar REE pattern. The mass magnetic susceptibility (Xlf) values of suspended sediments (28 to 1000 × 10^{-8} m^3 kg^{-1}) indicate variable concentration of heavy metals. The Xlf values show faint positive correlation with their respective bulk heavy metal contents in a limited sample population. The present study comprising geochemical analysis and first magnetic measurement data of suspended sediments in water samples shows a strongly polluted nature of Ganga and Yamuna Rivers at Allahabad contrary to the previous report mainly caused by overtly polluted city sewage water.

Keywords Sewage water · Ganga and Yamuna Rivers · Suspended sediments · Geochemistry · Magnetic susceptibility

M. Chakarvorty (✉) · A. K. Dwivedi · S. Kumar · A. Niyogi · M. Usmani · J. K. Pati
Department of Earth and Planetary Sciences, Nehru Science Centre, University of Allahabad, Allahabad 211 002, India
e-mail: mchakarvorty@gmail.com

A. D. Shukla
Physical Research Laboratory, Thaltej Campus, Ahmedabad 380 009, India

Introduction

Major rivers worldwide are threatened by effluent discharge from the sewage systems due to ever increasing anthropogenic activities in the nearby urban centers and catchment areas (Vörösmarty et al. 2000; Jackson et al. 2001; Singh et al. 2002; Vörösmarty et al. 2003; Dudgeon et al. 2006; Boran and Altinok 2010; Huang et al. 2010; Vörösmarty et al. 2010; Zhang et al. 2014), primarily due to the release of the industrial waste (Poulichet et al. 2002; Mauskar 2008; Cazenave et al. 2014; Klaver et al. 2014) through sewage networks leading to large-scale ecological imbalance (Vörösmarty et al. 2003; Abell et al. 2008; IUCN 2010). A solution to this universal problem requires a paradigm shift in our approach to quantify the level of ecotoxicity for major rivers so that the remedial measures are better and rapidly implemented in local to regional scales (Jain 2002; Wang et al. 2007). The geochemistry of river water and associated sediments in various forms (suspended, dissolved, and bed load)

are routinely investigated to monitor and assess river health (Chakrapani and Subramanian 1996; Konhauser et al. 1997; Dalai et al. 2004 and references therein). In recent years, magnetic measurements have evolved as rapid, nondestructive, cost-effective, and accurate technique to study heavy metal pollution in river sediments worldwide effectively involving large number of samples with variable mass (Sangonde et al. 2001; Chaparro et al. 2011; Chaparro et al. 2013 and references therein).

In India, two major rivers originating from the Himalayas, Ganga, and Yamuna are in the verge of a mega-environmental disaster due to pollutant discharge at various locations such as New Delhi, (Singh et al. 2002; Bhattacharya et al. 2015), Mathura (Bhargava 2006), Kannauj (Das 2011), Agra (Singh et al. 2002), Kanpur (Singh et al. 2002), Allahabad (Singh et al. 2002; Gupta et al. 2009), Mirzapur (Sharma et al. 1992; Srivastava et al. 1993), Varanasi (Pandey et al. 2010; Rai et al. 2010), Patna and Kolkata (Kar et al. 2008; Akhtar et al. 2010; Manna et al. 2013), and also at various locations along the respective river courses (Ajmal et al. 1985; Subramanian et al. 1985; Saikia et al. 1988; Singh and Singh, 2007; Rai et al. 2010; Singh et al. 2012). The effluents are released from various industrial units (leather, paint and pigment, paper pulp, domestic sewage, metal-alloy industry, electroplating and battery-manufacturing units; Trivedi 2010; Samanta 2013). The veracity of the problem in the study area has been highlighted on the basis of various studies comprising photosynthetic activity in the river water to assess its effect on river ecology (Tare et al. 2003), bioaccumulation and distribution of heavy metals in river sediments (Singh et al. 2002; Singh et al. 2003; Akhtar et al. 2010), and impact on fish species (Gupta et al. 2009; Samanta 2013), water quality degradation (Trivedi 2010; Sanghi 2014; Sharma et al. 2014), and decline in aquatic biodiversity (Birch et al. 2001; Gupta et al. 2009). However, the magnitude of degradation of aquatic environment due to local-scale anthropogenic activities has so far been evaluated based on river water geochemistry and impact assessment on aquatic life forms.

The Ganga and Yamuna Rivers flow over a predominantly felsic bedrock impoverished in heavy metals, dissecting the Himalayan foothills, penninsular India and Indo-Gangetic alluvium over a distance of about 1100 and 1353 km, respectively, and meet at Allahabad (Fig. 1; Sangam: 25° 25′ 27.41″ N and 81° 53′ 19.85″ E). Although the city is not overtly industrialized, it becomes a place of mass congregation of epic proportion when tens of millions of Hindus every year gather to perform religious rituals in the banks of river Ganga (at Sangam, Allahabad; Fig. 2a) for about a month (December–January) leading to large-scale irreversible mass pollution of the river water. In addition, everyday religious offerings (like coconuts, flowers, leaves, clothing, statues, dairy products, and oil lamps), polythene bags, ash from human cremations, dead bodies, and animal carcasses are also dumped into the river (Fig. 2b). A number of small-scale industries, such as paint, food, polythene, soap, chemical, printing, vehicle, paper, and battery industries are operating within the settlement areas of Allahabad city (Fig. 1) which contribute various forms of waste (including chemical effluents) and pollutants into the city sewage system (Fig. 2c) largely untreated (Fig. 2d). Although the water of Ganges at Sangam, Allahabad is revered as holy, yet the level of pollution, pollutant chemistry, and the possible source with respect to the city sewage systems are not known. The particulate matters in stream water are carried in suspension, in dissolved state, and as bed load. The mass of suspended particulate matter in riverine systems is mainly dependent on natural and anthropogenic parameters (Viers et al. 2009).

The present study is aimed to monitor the physicochemical properties of suspended sediments in sewage and mixed water samples from different parts of Allahabad city. An attempt has been made to use magnetic susceptibility measurement of suspended sediments present in water samples as a rapid, cost-effective, and nondestructive technique to estimate the heavy metal concentration comprising comparatively large number of samples in conjunction with sample analysis by traditional geochemical method with limited number of samples. In addition, the baneful effect of heavy metal toxicity and possible role of anthropogenic pollutants on REE content of suspended sediments present in water samples have also been investigated.

Materials and method

Study area

The city of Allahabad is spread over 70-km^2 area in the northern Indian state of Uttar Pradesh (Fig. 1). It is a famous center of pilgrimage with a local

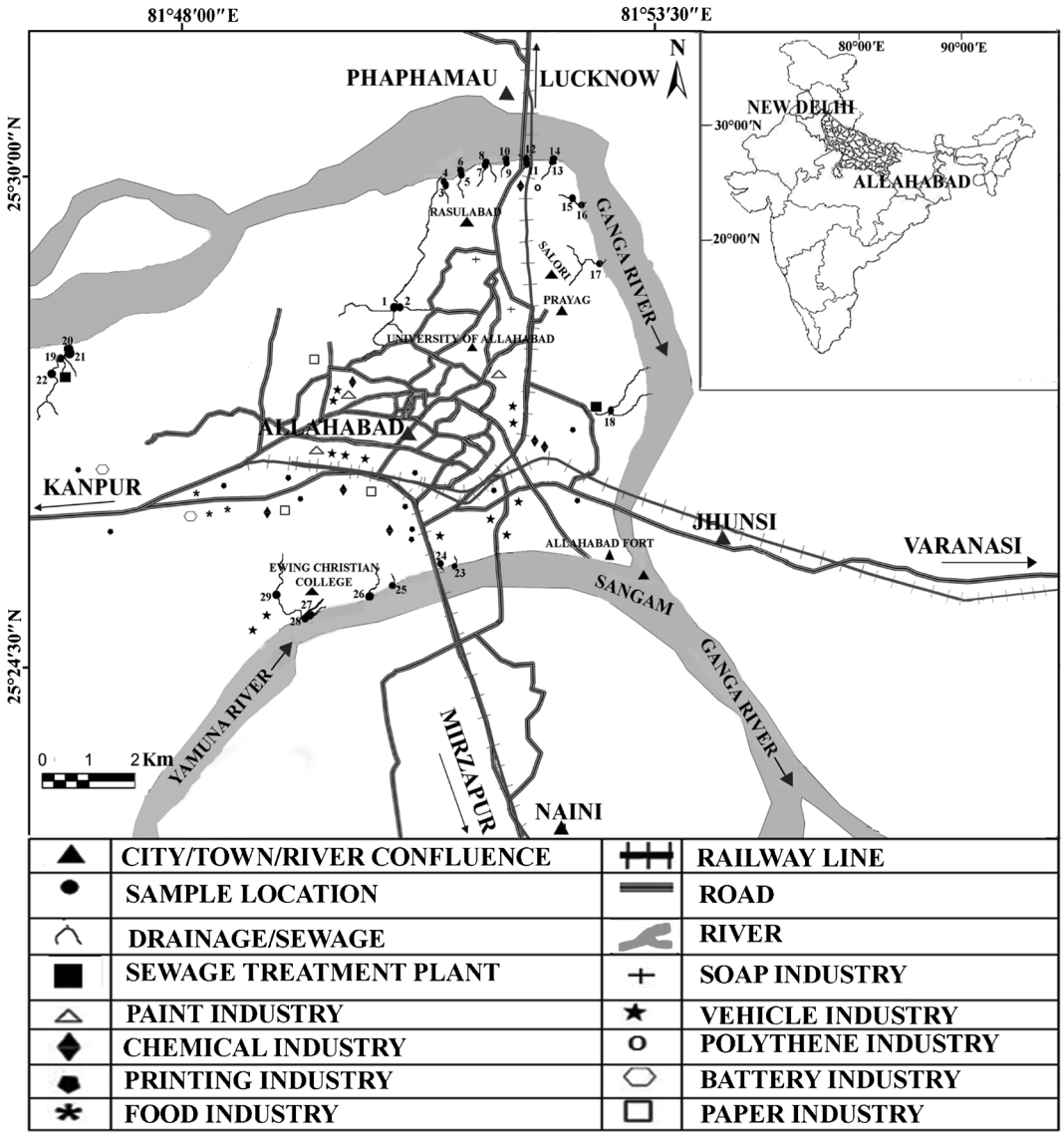

Fig. 1 Schematic map of the study area Allahabad city with sampling location geo-coded points

population of about 1.2 million inhabitants. It is situated at the confluence of the Ganga and Yamuna Rivers and at an elevation of 98 m from the mean sea level. Of the nine major cities of north India affected by winter fog (Chandigarh, New Delhi, Agra, Mathura, Kanpur, Allahabad, Varanasi, Lucknow, and Jaipur), Allahabad has the least numbers of industries. The Allahabad city occurs within the foreland depositional basin of Ganga plain (Central Alluvial Plain) flanking the Vindhyan Supergroup in the south. The Quaternary sediments comprising sand, silt, clay, and calcretes mainly of fluvial origin overlie sandstone (areanites) belonging to Chitrakoot Formation, Banda Group (Vindhyan Supergroup) in the study area (Kumar 2005). The sediments in this area are the youngest in the Ganga Plain. The artefacts observed within brown sand close to Allahabad (study area) reveal dates between 10,345 ± 110 and 19,715 ± 340 years BP (Sharma 1975). The depth to basement (Chitrakoot Formation) varies between 188 and 278 m (Pati et al. 2008a).

Sampling and analytical methods

Twenty nine water samples are collected in 1-l capacity Teflon® bottles from 29 mappable major sewages and confluence sites between the rivers and

Fig. 2 **a** Mass bathing of ambitious quantity of tens of millions of Hindus every year gather to purify their souls in the banks of river Ganga (Courtesy: Subrata Bal). **b** The human body is thrown away with other wastes to decay in river water. **c** The sewage water chiefly consists of nondegradable plastic and it is the major source of water pollution. **d** Confluence of nala and Ganga river showing mixed source of Ganga river with sewage water

sewages (two from each site) in parts of Allahabad city on 4 days between April 14 and May 5, 2013. The cleaned Teflon® bottles are gently dipped into the water body and filled to the tip and capped. Care is taken to collect sewage water far removed from the sewage and river confluence site. The sampling distance from banks of the major rivers varies between 20 and 900 m. The samples of the sewage are collected from the sites before the break-in topographic slope in the upstream direction in order to eliminate the possible influence of river water. The sewage and river confluence sites are also chosen as representative sampling sites. Number of small-scale industries, such as paint, food, polythene, soap, chemical, printing, vehicle, paper, and battery industries, contribute to various forms of waste (including chemical effluents), and pollutants into the city sewage system are the major contamination sources in the study area. These small-scale industries vis-à-vis possible source locations as well as sampling points have been shown in Fig. 1. The mixed water samples are collected close to the river bank at the confluence site between sewage and river water. The in situ measurements of water temperature (29 and 33 °C) and pH (5.9–8) are summarized in Table 1. The summer months are chosen to avoid dilution effect observed during rainy and post-rainy periods (Singh et al. 2002; Sharma et al. 2014). One time sampling method, similar to Gupta et al. (2014), has been adopted during the present study to demonstrate the effectiveness of magnetic measurement to quantify heavy metal pollution. Twenty samples belong to sewage systems, and nine are from the river and sewage confluence sites (Fig. 1). The water samples are filtered using ashless Whatman® filter paper (Grade 40; pore size 8 μm). Filtered water is discarded and the residual sediments are oven dried at 100 °C for an hour, and their respective weights are measured using a Mettler Toledo analytical balance (AB104-S, Germany). Thereafter, the samples are subjected to magnetic susceptibility measurement and chemical analysis.

Table 1 Sampling details of suspended sediments samples from Allahabad city

Sl. no.	Sample no.	Sample type	Date of collection	Location		Site area	pH	*T* (° C)
				Latitude	Longitude			
1	SW1	Sewage water	14/4/2013	25° 28′ 33.2″ N	81° 50′ 27″ E	Beli gaon	7.8	29
2	SW 2	Sewage water	14/4/2013	25° 28′ 33.2″ N	81° 50′ 31.3′ E	Beli gaon	5.9	29
3	SW 3	Sewage water	14/4/2013	25° 29′ 54.7″ N	81° 51′ 0.88″ E	Mehndauri	7.9	29
4	GMW4	Mixed water	14/4/2013	25° 29′ 55.5″ N	81° 50′ 59.8″ E	Mehndauri	5.9	29
5	SW 5	Sewage water	14/4/2013	25° 30′ 4.8″ N	81° 5111.5″ E	Rasolabad	7.7	29
6	GMW 6	Mixed water	14/4/2013	25° 30′ 5.6″ N	81° 51′ 11.3″ E	Rasolabad	8	29
7	SW 7	Sewage water	14/4/2013	25° 30′ 12.9″ N	81° 51′ 32.1″ E	Taliarganj	7.8	29
8	GMW 8	Mixed water	14/4/2013	25° 30′ 13.4″ N	81° 5131.8″ E	Taliarganj	8.1	29
9	SW 9	Sewage water	14/4/2013	25° 28′ 33.2″ N	81° 50′ 27″ E	Taliarganj	7.5	29
10	GMW 10	Mixed water	14/4/2013	25° 28′ 33.2″ N	81° 50′ 27″ E	Taliarganj	7.9	29
11	SW 11	Sewage water	25/4/2013	25° 30′ 15.3″ N	81° 51″ 54.8″ E	Shanker Ghat	7.5	30
12	GMW 12	Mixed water	25/4/2013	25° 30′ 17.8″ N	81° 51′ 54.5″ E	Shanker Ghat	7	30
13	SW 13	Sewage water	25/4/2013	25° 30′ 11.4″ N	81° 52′ 18.7″ E	Shivkuti	8.5	30
14	GMW 14	Mixed water	25/4/2013	25° 30′ 13″ N	81° 52′ 18.8″ E	Shivkuti	8.6	30
15	SW 15	Sewage water	25/4/2013	25° 29′ 44.7″ N	81° 52′ 34.3″ E	Chetla	7.9	30
16	GMW 16	Mixed water	25/4/2013	25° 29′ 45.2″ N	81° 52′ 38.6″ E	Chetla	8	30
17	GMW 17	Mixed water	25/4/2013	25° 29′ 4″ N	81° 52′ 50.7″ E	Kailashpure	8	30
18	SW 18	Sewage water	25/4/2013	25° 27′ 27.1″ N	81° 53′ 0.8″ E	Daraganj	8.8	30
19	SW 19	Sewage water	25/4/2013	25° 28′ 33.2″ N	81° 50′ 27″ E	Dhoomanganj	7	33
20	GMW 20	Mixed water	25/4/2013	25° 28′ 33.2″ N	81° 50′ 27″ E	Dhoomanganj	7	33
21	SW 21	Sewage water	05/5/2013	25° 27′ 57.3″ N	81° 46′ 37.9″ E	Dhoomanganj	7	33
22	SW 22	Sewage water	5/5/2013	25° 27′ 57.7″ N	81° 46′ 38″ E	Dhoomanganj	8	33
23	GMW 23	Mixed water	05/5/2013	25° 27′ 56.1″ N	81° 46′ 35″ E	Yamuna Ghat	7	33
24	SW 24	Sewage water	05/5/2013	25° 27′ 45.4″ N	81° 46′ 26.3″ E	Yamuna Old Bridge	7	33
25	SW 25	Sewage water	05/5/2013	25° 25′ 38″ N	81° 51′ 9.6″ E	Dariyabad	7	33
26	SW 26	Sewage water	05/5/2013	25° 25′ 39.4″ N	81° 50′ 57.1″ E	Dariyabad	7	33
27	YMW 27	Mixed water	05/5/2013	25° 25′ 26.1″ N	81° 50′ 24.9″ E	Chacharnala, Kareli	7	33
28	YMW 28	Mixed water	05/5/2013	25° 25′ 21.6″ N	81° 50′ 12.1″ E	Chacharnala, Kareli	7	33
29	SW 29	Sewage water	05/5/2013	25° 25′ 7.7″ N	81° 49′ 31.3″ E	Karamat chowki	7.5	33

SW suspended sediments in sewage water, *GMW* Ganga mixed (river and sewage mixed water sample at the confluence) water suspended sediments, *YMW* Yamuna mixed (river and sewage mixed water sample at the confluence) water suspended sediment

Magnetic susceptibility measurements

The magnetic susceptibility measurement of suspended sediment samples are made using a Bartington MS2 magnetic susceptibility meter attached to a MS2B Dual Frequency Sensor (UK). In order to avoid accidental errors, the mean value of three individual measurements (mean of three individual values ±0.02) are considered for every reported figure (Table 2). The magnetic susceptibility measurements are based on high frequency and low frequency modes (0.47 and 4.7 KHz; Chakarvorty et al. 2014).

Chemical analysis

The variation in magnetic susceptibility values and sample locations are taken into account in selecting eight representative samples for their chemical

Table 2 Magnetic susceptibility measurements of suspended sediments in sewage and mixed water samples

S. no.	Sample no.	Weight of suspended sediment (g)	Mass magnetic susceptibility, low frequency (LF)	Mass magnetic susceptibility, high frequency (HF)
1	SW1	0.061	147.54	114
2	GMW 2	0.013	230	153
3	SW 3	0.011	181	90.9
4	GMW 4	0.013	307	153.84
5	SW 5	0.015	133	66.6
6	GMW 6	0.014	285	142.85
7	SW 7	0.01	300	200
8	GMW 8	0.506	37	9.88
9	SW 9	0.036	250	83.33
10	GMW 10	0.019	315	52.63
11	SW 11	0.188	42	31.91
12	GMW 12	0.012	166	83.33
13	SW 13	0.006	166	166.66
14	GMW 14	0.005	200	100
15	SW 15	0.101	178.8	118.81
16	GMW 16	0.072	138.2	97.22
17	SW 17	0.002	500	350
18	SW 18	0.015	133.33	66.66
19	SW 19	0.02	1000	500
20	GMW 20	0.002	50	10
21	SW 21	0.02	400	100
22	GMW 22	0.316	28.48	22.15
23	SW 23	0.011	400	200.9
24	YMW 24	0.005	363.63	200
25	SW 25	0.039	102.56	25.64
26	YMW 26	0.076	78.94	39.47
27	SW27	0.007	571.42	428.57
28	YMW 28	0.01	300	200
29	SW 29	0.02	178	140

analysis. The samples are analyzed for various elements using a Quadruple Inductively Coupled Plasma Mass Spectrometer (Q-ICP-MS) Thermoelectron X-series^{II} ICPMS housed at Planetary Sciences Exploration Program (PLANEX), Physical Research Laboratory (PRL), Ahmedabad, India. The analysis were carried out following standard protocol of analyzing trace elements in rocks and sediments after dissolving the collected sediments (Shukla 2011; Ray et al. 2008). The samples were dissolved in Teflon vessels using ultra-pure HF (0.5 ml), HCl (0.5 ml), and HNO_3 (1.5 ml) acids in a microwave digestion system (Milestone, USA). The final solution about 50 ml was prepared in 5 % HNO_3. For the analysis of the concentrations of elements, calibration curves were drawn for each element (maximum up to 50 ppb) using USGS rock standard (BHVO-2) with a reagent blank prepared in similar way as for the sample. The detection limits reproducibility (external precision) based on repeated analysis of a sample found to be better than 2 % at 2 σ level for most of the trace elements. The accuracy of the data was performed by analyzing another aliquot (solution) of BHVO-2 at regular interval during the analysis and found to agree well with the reported values (Shukla 2011).

Statistical analysis

Statistical analysis of the geochemical data using SPSS17 software is conducted to establish correlation between toxic heavy metals with mass magnetic susceptibility values. The enrichment ratio (ER) is used in the present study to delineate the anomalous heavy metal content in suspended sediments introduced due to anthropogenic activities with respect to elemental concentration in crustal source (Salomons and Förstner 1984; Suther et al. 2009). The upper continental crust (UCC) data (after Taylor and McLennan 1985) is used as reference to calculate the ER and geoaccumulation index (Igeo) in order to ascertain the pollution level and compare with worldwide database (Förstner and Müller 1981; Suther et al. 2009). The calculation of ER and Igeo is based on the following formulae:

For enrichment ratio (ER),

$$ER = C_{metal}/C_{UCC}$$

where C_{metal} represents the concentration of measured element in the sample and C_{UCC} denotes the average concentration of the UCC. The value of ER < 1 suggests the crustal input and >1 is indicative of anthropogenic source (Rasmussen et al. 1998).

For geoaccumulation index (Igeo),

$$Igeo = Log_2 \{(C_n)/1.5(B_n)\}$$

where C_n is the concentration of measured element in sample and B_n refers to the average concentration of UCC used as background value. The value of Igeo is characterized into seven different classes (Muller 1969). The classes include (1) Igeo ≤ 0 (unpolluted), (2) 0 ≤ Igeo ≤ 1 (unpolluted to moderately polluted), (3) 1 ≤ Igeo ≤ 2 (moderately polluted), (4) 2 ≤ Igeo ≤ 3 (moderately to heavily polluted), (5) 3 ≤ Igeo ≤ 4 (heavily polluted), (6) 4 ≤ Igeo ≤ 5 (heavily to extremely polluted), and (7) Igeo ≥ 5 (extremely polluted) referring to the degree of pollution for a given element (Fig. 3) (Müller 1979; Müller 1981; Mohiuddin et al. 2010).

Results and discussion

Magnetic susceptibility of suspended sediments

The magnetic susceptibility data of 29 samples with their respective absolute weights is summarized in Table 2. The Xlf measurements provide a rough measure in terms of the concentration of all magnetic minerals having high magnetic remanence and Xlf values of the suspended sediments obtained during the present study range between 28.48 and 1000 × 10^{-8} m^3 kg^{-1}. The Xlf of suspended sediments in sewage water (42–1000 × 10^{-8} m^3 kg^{-1}) is more than that of mixed water (28–408 × 10^{-8} m^3 kg^{-1}). The Xlf values of suspended sediments in sewage water increase between 178 and 1000 × 10^{-8} m^3 kg^{-1} in densely populated areas (like Beligaon, Mutthiganj, and near Govindpur Colony). On the other hand, the Xlf values decrease (133–363 × 10^{-8} m^3 kg^{-1}) in sewage samples collected from sparsely populated areas and in suspended sediments obtained from mixed water samples from the banks of Ganga (near Phapamau Bridge, Teliarganj) and Yamuna (near Kydganj) rivers.

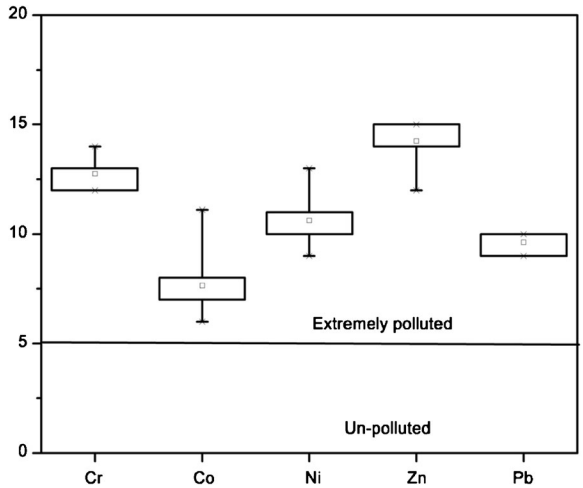

Fig. 3 Geoaccumulation index (after Müller 1979) of trace metals in suspended sediments extremely polluted

The correlation coefficients between six metals and their respective Xlf values for eight samples are shown in Table 4. Previous studies worldwide have shown a direct correlation between magnetic susceptibility values with heavy metals content in suspended sediments as well as water samples (Petrovsky et al. 1998; Schmidt et al. 2005; Chaparro et al. 2008). In the present study, all metals, except Zn and Pb, show positive correlation with Xlf. A further analysis showed a positive correlation between Pb and Zn in terms of their elemental concentrations, but they show a weak negative correlation ($R^2 = 0.06$) with bulk Xlf of the samples. On the other hand, the remaining elements (V + Cr + Ni + Mn) show a positive correlation ($R^2 = 0.27$) with

bulk Xlf values. In addition, the negative correlation shown by Pb and Zn with Xlf can be explained by their negative Xlf values (−0.11 and -0.14×10^{-8} m^3 kg^{-1}, respectively; modified after Börnstein 1986) compared to positive magnetic susceptibility values of V, Cr, Ni, and Mn (5.59, 3.21, ferromagnetic and 9.30×10^{-8} m^3 kg^{-1}, respectively). An interesting observation made during the present study suggests that while comparing magnetic susceptibility of heavy metals with their respective mass concentrations, a better correlation can be arrived only when Pb and Zn contents are relatively depleted in the samples.

Trace elements and REE geochemistry

The geochemical analyses of eight representative suspended sediment samples by ICP-MS technique are summarized in Table 3**.** The samples for geochemical analysis are chosen based on their respective variable magnetic susceptibility values. The elements analyzed include mostly trace elements and heavy metals (Ba, Pb, P, Ni, Cd, Co, V, Zn, Sc, Mn, Rb, Sr, Y, Zr, Cs, U, and Cr) including all rare earth elements (REE). The Igeo (Müller 1969) is calculated for five elements (Cr, Co, Ni, Zn, and Pb) as these heavy elements strongly correlate with anthropogenic activities and shown in box whisker plot (Fig. 4**)** with two fields separating the unpolluted domain from extremely polluted class**.** It also reflects the magnitude of heavy metal pollution in suspended sediments. Based on the index, the sediment quality of present study lies in extremely polluted class suggesting that suspended sediments are highly polluted with the aforesaid metals. The previous study reported Igeo for Co having minimal effect and plot in class 0 (unpolluted; Singh et al. 2002). Ni, Cr, and Pb exhibit moderately polluted effect belonging to class 3. Zn reflects moderately to highly polluted nature, typical of class 4. Cd occurs in class 6 suggesting very highly polluted nature and exerting maximum effect on the river sediments.

The anthropogenic input in the study area has been described with respect to its target source. The sample bearing number SW 1 (Table 3) shows high concentration of Mn and Zn due to discharge of effluents from battery and electroplating industries showing good correlation with respect to Xlf. The SW 5 sample shows the presence of Zn, Mn, and Pb which have been derived from chemical, polythene, and soap industries **(**Fig. 1**)**. The excessive concentration of Mn, Zn, and Cr is released from industries like chemical, polythene, paint, and dying in sample GMW 10. The location near Chetla (Fig. 1), where both sewage and mixed water (SW 15 and GMW 16) have been analyzed, shows high absorption rate of heavy metals like Zn, Mn, Cr, and Ni derived mainly from polythene, chemical, paint, and dying industries. The source of Mn, Zn, and Cr observed in sample SW 21 is mainly contributed by STPs (sewage treatment plants), battery, printing, and dying industries. The small-scale vehicular industries, welding units, battery, chemical, and paper factories in the study area are responsible for the anomalous heavy metal toxicity in samples SW 24 and YMW 28. The measured Xlf values of suspended sediment samples are consistent with the distribution of the pollutant sources in the study area.

ER for seven analyzed elements (Co, Mn, Pb, Ni, Cr, V, and Zn) is shown in Fig. 5. All metals show high enrichment with respect to the upper continental crust (UCC) values, and the ER increases in the following order: Co, Mn, Pb, Ni, Cr, V, and Zn. The average ER of heavy metals in the present study are Zn, 8.08; V, 1.25; Cr, 4.29; Ni, 2.53; Pb, 3.22; Mn, 0.79; and Co, 1.61). Singh et al. (2002) reported different values for some of the elements (Zn, 1.08; Cr, 1.90; Ni, 0.83; Pb, 1.12; Mn, 1.25; Co, 1.15) from the study area. Based on the above observations, it can be concluded that the increase in industrialization and anthropogenic activities in a span of 11 years have resulted in the elevated concentration of heavy metals in the river system.

Singh et al. (2002) reported the background values of some of the heavy metals in Ganga River sediments such as Mn 1715 ppm, Pb 23 ppm, Zn 106 ppm, Ni 46 ppm, Cr 150 ppm, and Co 21 ppm. In the present study, the Mn concentration in sewage and mixed water samples are variable (313–839 and 393–603 ppm, respectively). The acceptable limit of Mn content in drinking water is 400 ppm (WHO 2008). The Igeo of Mn (17–19) calculated during the present study suggests extremely polluted nature of sewage and mixed water. The source of Mn in sewage water may be derived from landfills sites and pigment industry. The major anthropogenic sources of manganese include municipal wastewater discharges, sewage sludge, and emissions from alloy industries. The concentration of Pb in sewage (48–77 ppm) and mixed water (46–86 ppm) samples are variable. In drinking water, Pb content is about 10 ppm (WHO 2008). The Pb in sewage water is possibly derived from the anthropogenic sources (industrial and automobile sectors, waste processing, smelting

Table 3 Concentration of trace elements and REE in the suspended sediments from sewage water falls in to Ganga and Yamuna Rivers in contrast to other major word rivers, UCC, Ganga at Rishikesh, and North American Shale Standards

Sample no.	SW 1[a])	SW 5[a]	GMW 10[a]	SW 15[a]	GMW 16[a]	SW 21[a]	SW 24[a]	YMW 28[a]	Upper continental crust (UCC)[b]	World major rivers [b]	Ganga River[c]	North American Shale Composite Standard (NASC)[c]	Yamuna River[c]
Elemental concentration in ppm													
P	2407	6157	2335.5	4604	4808	3058.5	5086.5	3704	–	2010	–	–	–
Sc	52.74	32.65	47.98	62.01	53.65	109.5	17.21	17.56	14	18.2	0.00	14.9	–
V	73.92	45.27	63.85	61.47	101.55	93.6	71.38	90.23	60	129	0.00	–	104
Cr	87.19	79.58	87.33	187.15	147.85	246.25	266.8	101.5	35	130	0.00	124.5	85
Mn	451.5	313.8	392.1	395.55	603.75	839	408.15	524.45	620	1679	0.00	4646	–
Co	16.67	12.52	15.82	8.62	22.18	15.45	16.84	20.98	10	22.5	0.00	25.7	14
Ni	27.32	21	23.77	79.45	37.72	33.94	143.65	39.23	20	74.5	0.00	58	50
Pb	48.45	65.35	46.2	70.11	86.46	53.62	77.69	67.63	20	61.1	0.00	–	10
Zn	360.55	701	300.7	637.3	834.65	399.1	723.85	635.5	71	208	0.00	–	77
Rb	136.25	88.05	138.55	90	154.55	101	70.49	162.05	–	78.5	0.00	125	–
Sr	238.1	163.05	109.45	174.35	190.25	645	183.3	168.6	–	187	0.06	142	–
Y	14.12	11.88	16.42	11.84	14.59	28	4.7	20.29	22	21.9	0.0	–	20
Zr	55.59	28.53	30.1	52.81	83.55	122.05	58.77	61.59	–	160	0.00	200	–
Nb	12.43	6.71	9	9.8	17	6.99	10.36	11.49	–	13.5	0.00	–	–
Cs	13.95	6.97	11.08	7	14.23	9.1	5.12	14.49	–	6.25	0.00	5.16	–
Ba	675.2	309.3	402.15	411	599.6	480.75	400.65	480.25	550	522	0.02	636	–
Hf	1.65	0.84	0.9	1.66	2.55	2.95	1.78	1.86	–	4.04	–	6.3	–
Ta	1.1	0.57	0.74	0.82	1.45	0.71	0.83	0.92	–	1.27	0.00	1.12	–
U	5.08	6.23	4.69	7.49	8.03	3.3	9.05	5.40	–	3.3	0.002	2.66	–
REE (in ppm)													
La	19.31	19.87	35.67	20.92	25.16	51.43	2.95	32.67	30	37.4	34.50	31.1	22
Ce	61.61	37.98	67.06	48.77	58.38	92.23	22.15	64.67	64	73.6	70.40	66.7	43
Pr	5.9	4.32	7.75	5.09	5.26	14.65	1.58	7.32	7.1	7.9	8	5	5
Nd	23.89	16.65	30.1	19.72	20.34	65.76	6.59	28.21	26	32.2	30	27.4	17
Sm	5.35	3.12	5.58	4.07	3.51	12.63	1.74	5.4	4.5	6.12	6	5.59	3
Eu	1.06	0.63	0.99	0.73	0.71	3.64	0.42	1.13	0.88	1.29	0.99	1.18	0.6
Gd	4.92	2.97	4.9	3.58	3.39	11.45	2.05	4.94	3.8	5.2	5.30	5	4
Tb	0.69	0.41	0.65	0.49	0.45	1.4	0.28	0.7	0.64	0.82	0.82	0.85	0.5
Dy	4.08	2.3	3.47	2.89	2.53	7.71	1.74	4.05	3.5	4.25	5	–	3
Ho	0.76	0.46	0.65	0.53	0.51	1.43	0.32	0.79	0.8	0.88	0.95	–	0.7
Er	2.06	1.24	1.73	1.42	1.41	3.73	0.8	2.2	2.3	2.23	2.70	–	1.5

Table 3 (continued)

Sample no.	SW 1[a])	SW 5[a]	GMW 10[a]	SW 15[a]	GMW 16[a]	SW 21[a]	SW 24[a]	YMW 28[a]	Upper continental crust (UCC)[b]	World major rivers [b]	Ganga River[c]	North American Shale Composite Standard (NASC)[c]	Yamuna River[c]
Tm	0.27	0.18	0.22	0.18	0.2	0.46	0.11	0.31	0.33	0.38	0.42	–	0.2
Yb	2.04	1.22	1.64	1.32	1.46	3.11	0.83	2.27	2.2	2.11	2.70	3.06	1.5
Lu	0.26	0.16	0.21	0.16	0.22	0.41	0.1	0.3	0.32	0.35	0.41	0.46	0.2
Th	10.06	9.83	19.79	17.72	11.84	11.45	–	18.39	–	12.1	–	12.3	–
Eu/Eu*	0.63	0.6	0.58	0.58	0.63	0.93	0.68	0.67	0.65	0.7	0.54	0.66	0.70
Gd_N/Gd^*	1.06	1.44	1.08	1.06	1.11	1.16	1.18	1.06	0.97	0.97	0.99	1.00	–
Ce/Ce*	1.4	0.91	0.89	1.09	1.11	0.79	2.78	0.94	1.01	0.93	0.97	1.00	0.90
La_N/Yb_N	6.78	11.66	15.6	11.34	12.33	11.9	2.54	10.34	9.78	11.45	9.16	7.17	1.50

[a] Suspended sediments in sewage and river-sewage mixed water from the present study

[b] Average upper continental crust (Taylor and McLennan 1981) and chemical composition of world rivers (Viers et al. 2009)

[c] Average concentration of dissolved sediments in Ganga River at Rishikesh, India (Chakrapani 2005), North American Shale Composite (Gromet et al. 1984), and Yamuna River (Ramesh et al. 2000)

process, paint, and pigments industries). The concentration of Zn in sewage water is variable (360–723 ppm), and similar variation is observed in mixed water (300–834 ppm) as well. In Ganga and Yamuna Rivers, the concentration of Zn is 198 (Sangam, Allahabad) and 53 ppm (Agra), respectively (Ramesh et al. 2000), while the Zn content in drinking water is 5 ppm (WHO 2008). The suspended sediments in sewage and mixed waters are found to be extremely polluted based on Igeo of Zn (12–15; Fig. 4). The anomalous Zn content in Allahabad is mainly derived from industrial (smelters and electroplating industries) sources. The concentration of Ni in sewage water varies from 20 to 143 ppm, while in mixed water, the values are tightly constrained between 23 and 39 ppm. In drinking water, Ni is observed up to 70 ppm (WHO 2008). The Igeo of suspended samples (9–13) suggests extremely polluted nature of both sewage and mixed water. The elevated Ni content in sewage is possibly due to the contaminants released from electroplating units, battery-manufacturing units, and metal alloy industry. In general, the high concentration of Ni in river water is attributed to anthropogenic inputs (Qiao et al. 2013). The concentration of Cr in suspended sediments is moderate to very high and variable (79 to 266 ppm) considering the regional basement litho chemistry. The sewage water contains 79–266 ppm of Cr compared to 87–147 ppm observed in mixed water samples. In drinking water, Cr content is 50 ppm (WHO 2008). The Igeo for Cr is between 12 and 14 which suggest their extremely polluted characteristic. Source of Cr in city sewage system could be from septic systems, metal and alloy industries, leather works, and pigment industry located in the catchment area. Ramesh et al. (2000) also reported very high concentration of Cr (79–117 ppm) in Ganga River suspended sediments which is, however, lower than the Cr content reported in average suspended sediments of world major rivers (130 ppm; Viers et al. 2009). The concentration of V varies from 45 to 93 ppm in sewage water and between 63 and 90 ppm in river water. In drinking water, the V content is 0.1 ppm (Sepe et al. 2003). The anomalous V in sewage water may have been contributed by various industrial units, smelting plants, paint, and pigment industries situated in the study area (Fig. 1). The concentration of U varies from 3.3 to 9.9 ppm in sewage water, while in river water, it ranges between 4.6 and 8 ppm. In drinking water, the U content is 0.15 ppm (WHO 2008). The source of anomalous U in sewage water may have been derived from

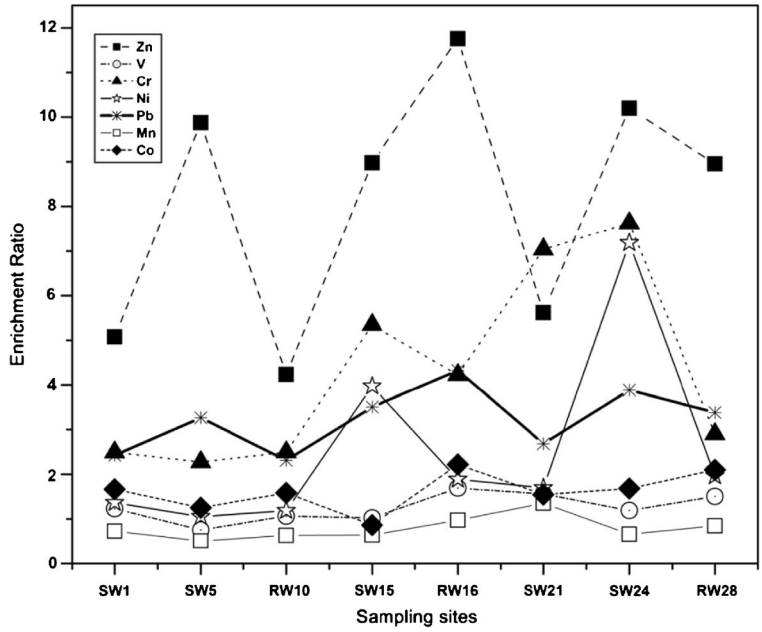

Fig. 4 Enrichments ratio normalized with UCC major toxic elements diagram showing less significant disparity between river water and sewage water in study area

various industrial units. The concentration of P varies from 2407 to 6157 ppm in sewage water, whereas in mixed water, it ranges between 2335.5 and 4808 ppm. In normal water, the P content is 480 ppm (Gromet et al. 1984). The eutrophication caused by over enrichment of P in water usually comes from agricultural and anthropogenic activities in aquatic ecosystem (Voutsa et al. 2001; Turner et al. 2003), and this possibly resulted in anomalous P content in sewage water observed during the present study.

The correlation coefficient between Pb and Zn is 0.96 at $P < 0.05$ level, which suggests their anomalous content, mainly derived from the widely distributed anthropogenic sources (paint, smelting, and battery industries). The correlation coefficients between respective metals are used to delineate anthropogenic contributions from natural sources in the sewage and mixed water (Table 4). A positive significant correlation at $P < 0.1$ level is observed in samples for element pairs, such as V-Mn (0.81) and Ni-Cr (0.73), and their elevated concentration compared to UCC abundance is mainly caused by increased industrial activities.

The UCC normalized multicationic plots (after Taylor and McLennan 1985; Fig. 5a–b) for the suspended sediments in sewage water and mixed water exhibit broadly similar patterns but individual samples in sewage water show major variations. The suspended sediments belonging to the mixed water samples show identical patterns with elevated Cs, Th, U, and REEs and depleted Rb, Ba, Ta, Nb, Sr, Hf, and Zr contents. The suspended sediments in sewage water show highly variable multicationic patterns with increased concentration of long-lived radionuclides (Cs, Th, and U) and depleted in Rb, Ba, Ta, Nb, Hf, Zr, and Y. In sewage samples, the Sr and REE contents exhibit major variation. The chondrite normalized (after Sun and McDonough 1989) REE pattern of eight representative suspended samples for 13 REEs is shown in (Fig. 6a–c), and the data is summarized in Table 3. The REE content of UCC (Taylor and McLennan 1985), Ganga River water (at Rishikesh; Chakrapani 2005), average water analysis of major world rivers (Viers et al. 2009), and NASC (Gromet et al. 1984) have been included for comparison. The REE data pertaining to suspended sediments of Yamuna River is after Ramesh et al. (2000). The sample selection for REE analysis was based on their mass magnetic susceptibility variation (Table 3).

The various factors, which govern the REE abundances in the natural water, include leaching, precipitation, colloidal transport, complexation, ion exchange, adsorption-desorption (Nakajima and Terakado 2003), concentration of colloids and pH (Gaillardet et al. 2004). The REE present in suspended sediments may come from the weathering of major minerals of bed rocks which may in turn influence their concentration in

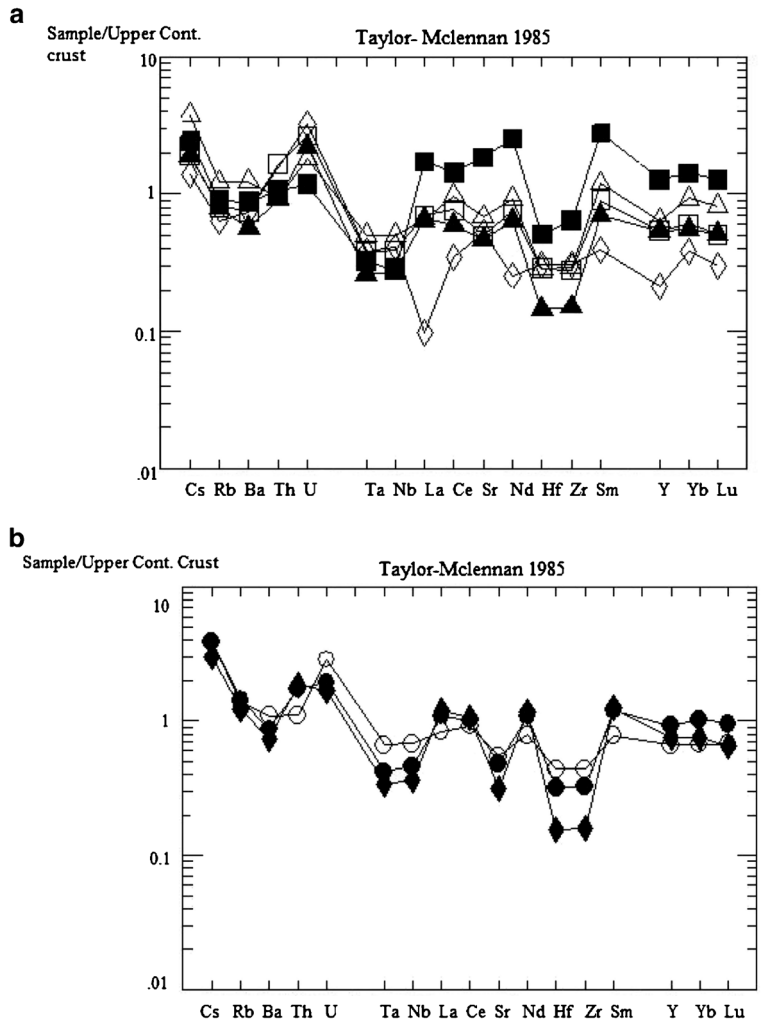

Fig. 5 Multi-cationic patterns of the suspended sediments from the **a** sewage water and **b** mixed water

suspended sediments. The ∑REEs in sewage water range between 41 and 270 ppm with an average concentration of 129 ppm, and for Ganga and Yamuna mixed water, it ranges from 123 to 160 ppm (average ∑REE = 142 ppm). The ∑LREE (total light rare earth elements) content in sewage water ranges from 33 to

Table 4 Pearson's correlation coefficients for the heavy metal concentrations with mass magnetic susceptibility of suspended sediments samples from Allahabad city

	Xlf	Zn	V	Cr	Ni	Pb	Mn
Xlf	1	−0.26	0.22	0.59	0.46	−0.14	0.32
Zn	−0.26	1	0.10	0.20	0.40	0.96**	−0.15
V	0.22	0.10	1	0.29	−0.06	0.26	0.81*
Cr	0.59	0.20	0.29	1	0.73*	0.34	0.45
Ni	0.46	0.40	−0.06	0.73*	1	0.50	−0.19
Pb	−0.14	0.96**	0.26	0.34	0.50	1	−0.03
Mn	0.32	−0.15	0.81*	0.45	−0.19	−0.03	1

*Correlation is significant at the 0.01 level (2-tailed); **Correlation is significant at the 0.05 level (2-tailed)

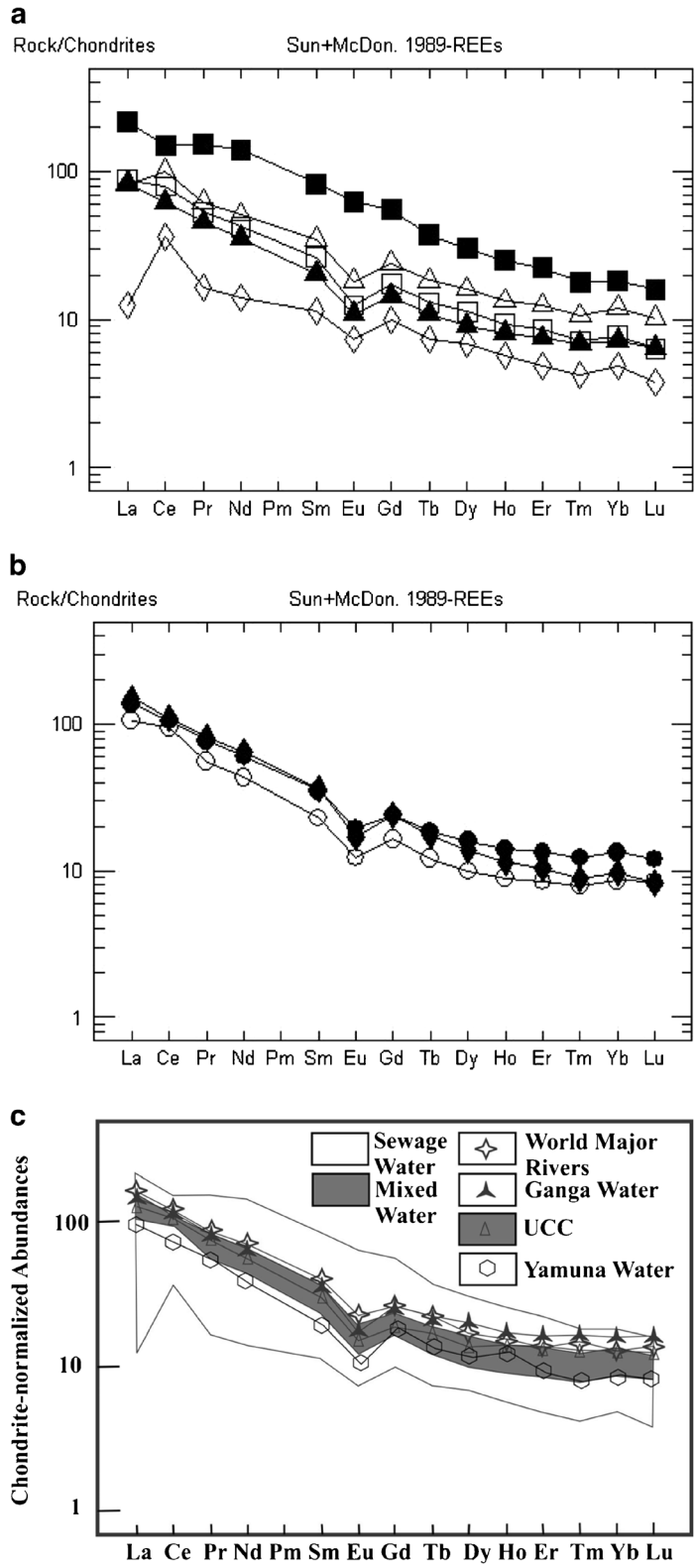

Fig. 6 Chondrite normalized REE patterns of the suspended sediments (present study) in samples from **a** sewage water and **b** mixed water; (**c**) chondrite normalized REE concentration in suspended sediments belonging to Ganga and Yamuna river water, world major river water, and elemental concentration in upper continental crust are compared with data obtained during the present study

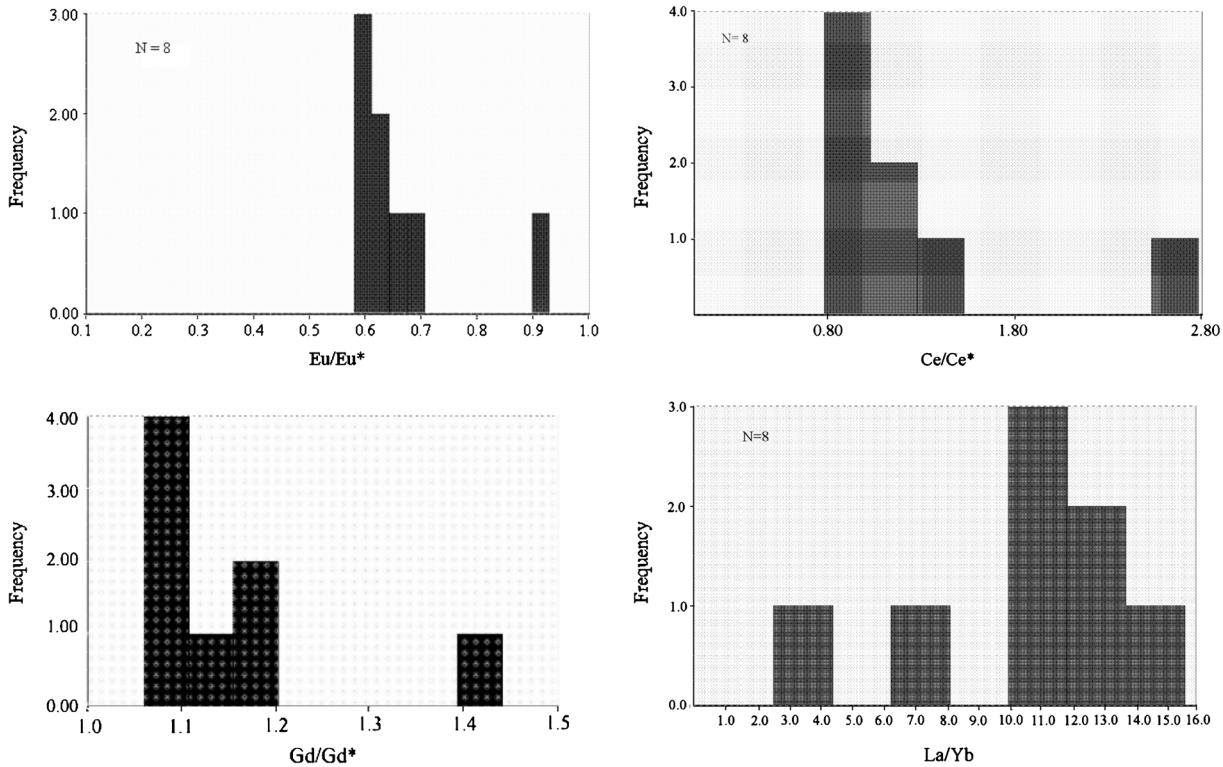

Fig. 7 Distribution of Ce, Eu, Gd, and La/Yb anomalies in suspended sediments of the sewage water falls into rivers Ganga and Yamuna

224 ppm, while in mixed water, they range between 109 and 140 ppm. The elevated ∑LREE values observed during the present study are similar to the earlier report from the bed rock samples (Bundelkhand granitoids; Pati et al. 2008b).

The suspended sediments analyzed during the present study show low to moderate degree of fractionated REE pattern (La_N/Yb_N = 2.54–12.33). All samples show negative Eu anomaly (Eu/Eu* = 0.58–0.93; average 0.66). River and sea water, in general, exhibit negative Eu anomaly (Martin and Meybeck 1979; Elderfield et al. 1990). The study area is situated close to the confluence of two major rivers (Fig. 2) having a large expanse of sandbars and flood plain deposits comprising sediments derived from the central India and the Himalayas mainly; the REE patterns compare well with the regional litho units (Chakarvorty et al. 2014). The cerium anomaly (Ce/Ce*) in the suspended sediment samples is variable (0.79 to 2.78). Four samples (SW 5, SW 21, GMW 16, and YMW 28) are showing negative Ce anomaly and the remaining four (SW 1, SW 15, SW 24, and GMW 10) exhibit positive anomalies. Positive Ce anomaly (Ce/Ce* = 2.78) indicates largely unfractionated to less fractionated (La_N/Yb_N = 2.54) nature of REE in a sample (SW 24) possibly due to deprived weathering and transport of suspended sediments and also by oxidation of suspended heavy metal rich particles formed in the stream water during the summer period (Ingri et al. 2000; Mao et al. 2014) wherein Ce^{3+} is converted to Ce^{4+} followed by subsequent stabilization of Fe-Mn oxyhydroxide complex (Pourret et al. 2008). The galadonium anomaly (Gd/Gd*) is calculated (Bau and Dulski 1996; Knappe et al. 1999; Tepe et al. 2014) to estimate anthropogenic pollutants in river water. The Gd/Gd* > 1 is suggestive of anthropogenic contribution (Knappe et al. 1999). The analyzed samples from the present study show positive Gd anomaly with Gd/Gd* ratio between 1.06 and 1.44 (Table 3; Fig. 7).

Conclusion

The present study was carried out to quantify the magnitude of pollution in urban sewage systems and its effect on water chemistry of Rivers Ganga and Yamuna at Allahabad city, India, using suspended sediment samples. The results of geochemical analysis and magnetic measurements suggest, in general, an

extremely polluted nature of city sewage and large river systems having varied enrichment ratio of heavy metals contrary to previous study. The heavy metals show relatively fair correlation with Xlf values and are derived from various small-scale industries occurring within the city area.

The ΣREE contents of samples analyzed during the present study show a significant variation with the available data pertaining to Ganga and Yamuna Rivers at upstream locations, average major world rivers, and UCC. The REE contents of sewage water samples are distinctly different, highly variable, and have a marked positive Gd anomaly suggesting a dominant role of anthropogenic activity. It is firmly established that the elevated heavy metal toxicity and ΣREE content observed in river waters at Allahabad is mainly contributed by anthropogenic and industrial pollutants released into the riverine systems through city sewage networks rather than prominent physical factors such as pH, carbonate ion concentration, and high erosion rate suggested earlier.

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