Spatial distribution and Anthropogenic imprints of La, Ce, Pr, Nd and Sm in Alluvium Sediments of Gangetic Plain, India

Yadav Jitendra Kumar[1,2]
1. Department of Geology, B. S. N. V. PG College, Lucknow-226 001, INDIA
2. Department of Geology, University of Lucknow, Lucknow-226 007, INDIA
jeetu068@gmail.com

Abstract

The primary study is based on anthropogenic imprints of Light Rare Earth Elements (LREE) such as La, Ce, Pr, Nd and Sm, which have become emerging contaminants due to their widespread use in high technologies in recent years. The main objective of present research is to investigate the spatial distribution and anthropogenic imprints of these elements in river sediments of the Gangetic Plain. In the Gomati River, there is a distinct downstream increase in the concentration of LREE, from 339 to 1349 µg/g, identified in the biotite of the mica-rich bedload sediments. Total average LREE content in suspended sediments of the Gomati (192.3 µg/g), the Sai (229.0 µg/g) and the Hindon (495 µg/g) rivers were observed to be higher than that of the Upper Continental Crust (131.6 µg/g), Average Sediments (122.9 µg/g), World Major Rivers Suspended Sediments (148.9 µg/g) and Post-Archean Australian Shale (166 µg/g).

The Hindon River's suspended sediment from highly urbanized centers at Ghaziabad (1519 µg/g) and Greater Noida (1377 µg/g) represented the extreme LREE levels. The Geo-accumulation index (Igeo) shows a toxicity trend in these sediments: Ce>Pr> La>Sm>Nd. Modern anthropogenic processes are responsible for the LREE enrichment in suspended river sediments, of nearly an order of magnitude higher than in the rivers of the Gangetic Plain. The increasing concentrations of these elements indicate the anthropogenic activities around rivers in urban centers and need for high- level research in the future to monitor them.

Keywords: Rare Earth Elements, Sediments, Geo-accumulation Index.

Introduction

Rare Earth Element (REE) have shown a sharp increase in use of high technology based activities in recent years such as agriculture and the industrial production of various technological devices, including computer hard drives, smartphones, fluorescent and light-emitting diode (LED) lights, flat screen televisions and electronic displays. However, these elements have been recently recognized as the potentially emerging pollutants in rivers system[3,4,7,12,13,41,42]. REE concentrations in sediments can be used to trace the recycling of the continental crust[37] and to assess anthropogenic impacts on rivers[13,39]. According to International Union of Pure and Applied Chemistry, REE are the chemically coherent group of 15 elements with similar physicochemical characteristics with atomic numbers between Z=57 and Z=71.

The distribution pattern of these elements reflects the Oddo-Harkins rule; the even atomic-numbered elements are an order of magnitude more abundant and additionally highlighted by a larger number of isotopes[30]. Therefore, these properties are the basis for REE conventionally divided into two groups: Light Rare Earth Elements (LREE) are Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Promethium (Pm) and Samarium (Sm). These elements form a cohesive group of metallic elements that exhibit some unique and similar chemical properties, which are used in many modern and "green" technologies[8]. On the other hand, Heavy Rare Earth Elements (HREE) are Europium (Eu), Gadolinium (Gd), Terbium (Tb), Dysprosium (Dy), Holmium (Ho), Erbium (Er), Thulium (Tm), Ytterbium (Yb) and Lutetium (Lu).

The LREE are found in a higher amount in the environment than the HREE[20]. La, Ce, Pr, Nd and Sm are identified as 'new modern emerging micro contaminants' in our environmental systems, for which there are currently no regulations available for monitoring their presence[24]. They have been recently recognized as emerging pollutants in rivers system due to release of electronic waste in rivers. However, data regarding La, Ce, Pr, Nd and Sm fluxes in association with either bed or suspended are scarce[32]. The huge uses and application in fertilizers, nuclear plant accidents and neo-forming soil processes also enrich these elements[1]. These elements enter in the various components of our living environmental system through the disposal of consumer and industrial products, landfills of waste electronic and electrical equipment, use of fertilizers and animal feeds etc.

Recently, the Rhine River in Germany and the Netherlands carried the anthropogenic Lanthanum and other elements such as Ce, Pr, Nd and Sm as a dissolved micro-contaminant[14]. Zhang et al[43] investigated La, Ce, Pr, Nd and Sm toxicity in human population in South Jiangxi area (China) and identified many biomarkers such as total serum protein, albumin, triglycerides, immunoglobulin and

https://doi.org/10.25303/1810da022033

cholesterol having high concentrations in human population attributed due to their prolonged intake through food etc. An epidemiological investigation[10,44] shows that long term exposure of residents living around mining areas can cause neurological diseases such as motor and sensory impairments, neuro-degeneration, or neurosis and can also reduce intelligence and motor ability in children, can deposit in the fetal brain. They can also affect neural tube development in children and pregnant women in mining areas[17,40]. The LREE are emerging contaminants that attracted research attention due to their potential human and ecological risks, their high technology and industrial applications based uses shown in table 1. Therefore, there is a crucial need to acquire the additional data of chemical composition of river sediments for the assessment of ongoing environmental changes during the present Anthropocene Epoch[39].

Table 1
An overview of La, Ce, Pr, Nd and Sm in various high-technology and industrial applications[12].

Light Rare Earth Elements	Main Applications
La, Ce, Pr, Nd	Alloys
Nd, Pr	Medical imaging Permanent magnets
La, Ce, Pr, Nd	Auto catalysts
La, Ce	Petroleum refining
La, Ce, Pr, Nd	Ceramics, glass additives
La, Ce	Phosphors
La, Ce, Pr	Polishing compounds

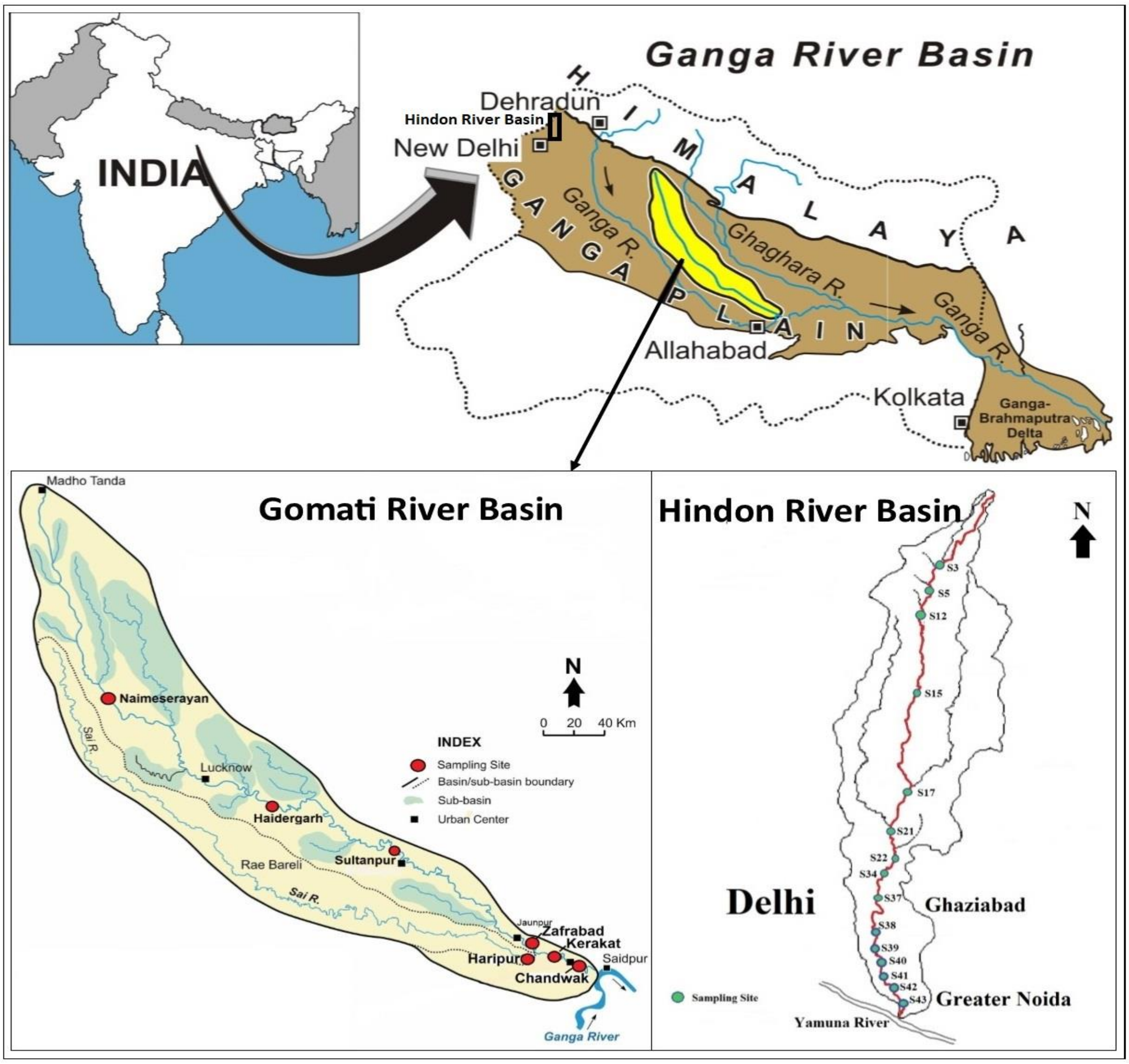

Figure 1: Study area map of Gangetic Plain showing the sampling sites; Gomati River (a tributary of the Ganga River), the Sai River (a tributary of the Gomati River), the Hindon River (a tributary of the Yamuna River)

Essentially, river sediments are a mixture of minerals and particles that are produced by the weathering of the drainage area. The geological, geochemical and environmental research groups benefited greatly from their chemical composition since it is frequently utilized to comprehend the anthropogenic (human induced activities) and geogenic (natural) processes that operate within the river basin[9,25,39]. The quantitative and qualitative analysis of these river sediments allow us to estimate anthropogenic influence, since these sediments offer large specific surface for the sorption of contaminants originating from the various human activities[26].

In the northern part of Indian sub-continent, the Gangetic Plain is one of the most densely populated regions of the world and supports the ~500 million human population[33]. The plain also supports the life of nearly ~700 million people with considerable socio-economic development supported by the accessibility of high technological applications. The indiscriminate expansion of urban centers and the unplanned disposal of waste materials generated by these urban centers are continuously degrading our natural living environment. Several urban centers have developed in a linear fashion along rivers of the plain mainly for the reasons of fresh water supply, strategic location and command over the agricultural wealth[28]. At the same time, these urban centers involve the extensive use of high-technology applications and traditional industries such as automotive, metallurgy and petroleum etc.

Consequently, the river basins draining the alluvial plain, are exposed to the anthropogenic La, Ce, Pr, Nd and Sm and therefore, act as a sink for other contaminants such as heavy metals and organic micropollutants[12]. The alluvial plain experiences a humid sub-tropical climate, characterized by four distinct seasons: the summer season (March-May), the monsoon season (June-September), the post-monsoon season (October-November) and the winter season (December-February). Geologically, the plain is made up of unconsolidated alluvial sediments basically derived from the Himalayan region. These alluvial sediments are well sorted silt and silty fine sand, representing muddy and sandy interfluve deposits[33].

Rivers draining in the Gangetic Plain have experienced similar lithological and climatic conditions but differential anthropogenic imprint in their sediments. A high-quality geochemical data base is needed in order to detect, monitor and evaluate the high technology related alterations under the La, Ce, Pr, Nd and Sm framework in these alluvial rivers (Gomati, Sai, Hindon and Ganga Rivers) (Fig. 1). It needs to be regarded as a fundamental facet of human knowledge with enormous significance for the Earth and biological sciences[38].

With this understanding, the rivers of the Gangetic Plain present an opportunity to study human-induced La, Ce, Pr, Nd and Sm contamination in the freshwater fluvial system. LREE fingerprints discovered in Gangetic Plain River sediments have been thoroughly examined in a geo-environmental research. The following are the primary objectives of the current investigation:

(**i**). To determine LREE concentration in bedload and suspended sediment of the Gomati and the Sai Rivers.
(**ii**). To investigate the anthropogenic influx of LREE in the downstream of Gomati River.
(**iii**). To assess the anthropogenic imprints of LREE on river sediments of the Gangetic Plain.

Material and Methods

Study Area: The 900-km long Gomati River is a groundwater fed river that cover drainage ~30,437 km^2 area in central part of the Gangetic Plain, north India. It is a largest tributary of the Ganga River and supports ~50 million human population residing in its drainage basin. The Sai River is the main tributary and drains nearly one-third part of the Gomati River Basin (GRB). The Hindon River is a 400-km long tributary of the Yamuna River and drains an area of ~7,083 km^2 in northern part of the Gangetic Plain. Mishra et al[22] reported the river water quality as severely polluted by untreated wastewater from industries and municipal sources. The La, Ce, Pr, Nd and Sm concentrations in its flood (suspended) sediments were reported by Mondal et al[23]. The La, Ce, Pr, Nd and Sm concentrations in Bedload and suspended sediments of the Himalayan and Ganga Alluvial Plain rivers showed the anthropogenic imprints La, Ce, Pr, Nd and Sm[1,5,18,27,29,35,36].

Sampling sites: The river sediment samples of the Sai River were collected from Haripur (confluence of Gomati and Sai River). In the Gomati River, two sampling sites Zafrabad and Kerakat representing before and after the confluence with the Sai River, were selected. The two sets of sediment samples (bedload and suspended sediment) were collected from these three sampling sites (Fig. 1). The samples of Biotite separated from bedload, were taken from four sampling sites namely Naimeserayan, Haidergarh, Sultanpur and Chandwak for determining downstream variation of La, Ce, Pr, Nd and Sm in the basin.

In the Gomati River Sediment, quartz, mica and feldspar are the common silicate minerals that significantly constitute (>80%) the bedload sand fraction[15]. In terms of natural withstanding, biotite and Ca-plagioclase are the two least resistant to chemical weathering minerals present in the bedload sediments. Biotite is one to two orders of magnitude of lower weathering resistance than muscovite, K-feldspar, Na-feldspar and hornblende[16].

Analytical Procedure: All the river sediments (bedload and suspended sediments) for the La, Ce, Pr, Nd and Sm analysis were collected in the zip locked polybag and samples were dried in the oven at a temperature of about 50-60°C, overnight. After that samples were prepared for further geochemical analysis such as drying, grinding, weighing and digestion in Geochemical Laboratory of the Birbal Sahni Institute Palaeosciences, Lucknow. All the oven-dry sediment samples were crushed and powdered by a porcelain mortar (disc mill Retsch RS 200), followed by a centrifugal ball mill. The 30 mg powdered samples were kept in a clean dried PTFE Teflon tube. Each sample was moistened with a few drops of ultra-pure water. Thereafter, each sample was completely dissolved by acid digestion using ultrapure (HNO_3-HCl-HF; 2:1:1 ratio) acids and Milli-Q water.

The La, Ce, Pr, Nd and Sm analysis was carried by Inductively Coupled Plasma Mass Spectrometer (ICP-MS: Perkin Elmer, ELAN DRC-e) in the lab. Reference materials, internal standards and analytical blanks were used for quality control for the La, Ce, Pr, Nd and Sm analysis during the digestion processes. Three types of reference materials named SGR-1b (Shale Green River), RGM (Rhyolite Glass Mountain) and SCO-1 (Cody Shale) from Standard United States Geological Survey (Supplementary table A1) for the precision of ICP-MS data proved better than ±6% RSD for all LREE analysis. Precision was always better than 6 to 10 % RSD.

Supplementary Table A1
Standard used during analysis of La, Ce, Pr, Nd and Sm. (Note: #Concentration obtain of Present study after ICP-MS analysis, **Universal standard Concentrations, DNA= Data Not Available).

S.N.	REE	SGR-1B#	SGR-1B**	RGM-2#	RGM-2**	SCO-1#	SCO-1**
1.	La	18.53	20 ±1.8	24.67	25 ±3	28.30	30 ±1
2.	Ce	35.60	36 ±4	49.09	DNA	54.57	DNA
3.	Pr	3.94	DNA	5.58	5 ±0.2	6.49	6.6
4.	Nd	14.20	16 ±1.7	20.01	20 ±1	24.73	26 ±2
5.	Sm	2.59	2.7 ±0.3	4.22	4 ±0.2	4.78	DNA

Table 2
The La, Ce, Pr, Nd, Sm and ∑LREE concentration in the bedload and suspended sediments of rivers draining Himalayan Region (HR), Ganga Alluvial Plain (GAP), Present Study (Gomati and Sai rivers) along with Global standards [Upper Continental Crust (UCC), Post-Archean Australian Shale (PAAS), Average Sediments (AS), World Major Rivers Suspended Sediments (WMRSS) and World Average River Silt (WARS)].
Note: DNA; Data Not Available.

Regions	Rivers	Sediment Type	La	Ce	Pr	Nd	Sm	∑LREE	References
HR	Ganga (n=11)	Suspended	21.0	40.0	4.9	15.2	3.3	83.0	29
"	Yamuna (n=08)	"	22.0	43.0	5.0	17.0	3.0	90.0	"
"	Bramhaputra (n=14)	"	20.7	41.0	4.8	15.0	3.2	86.0	"
"	Padma (n=04)	"	29.0	58.0	7.0	22.0	4.0	120.0	"
"	Meghna (n=09)	"	27.0	52.0	6.0	20.0	4.0	109.0	"
"	Ganga (n=01)	Suspended	34.5	70.4	8.09	30.1	6.1	149.1	5
"	Bhagirathi (n=01)	Suspended	37.1	79.5	9.0	32.9	7.0	165.5	36
"	Alaknanda (n=01)	"	29.9	60.4	6.9	25.0	4.9	127.0	"
"	Ganga (n=01)	"	34.5	70.4	8.1	30.1	6.1	149.2	"
"	Bhagirathi (n=05)	Bedload	28.3	59.8	DNA	26.1	6.0	120.1	"
"	Alaknanda (n=03)	"	34.6	71.7	DNA	30.4	6.2	142.8	"
"	Ganga (n=03)	"	31.9	65.5	DNA	27.7	5.7	130.7	"
"	Ganga (n=02)	"	37.9	76.5	8.0	31.2	6.7	160.3	27
GAP	Ganga (n=07)	Bedload	22.9	44.9	DNA	19.9	4.6	141.4	35
"	Ganga (n=06)	Suspended	38.2	83.9	9.1	33.5	6.6	171.2	11
"	Ganga (n=02)	Suspended	34.4	68.6	7.2	29.7	6.1	145.9	18
"	Gomati (n=02)	Suspended	45.35	91.2	10.2	38	7.45	192.3	Present study
"	"	Bedlod	25.7	51.5	5.8	21.5	4.15	108.6	"
"	Sai (n=01)	Suspended	54	108.6	12.1	45.5	8.8	229.0	"
"	"	Bedlod	35.6	72.1	8.1	29.6	5.8	151.2	"
Global	UCC	"	30	64	7.1	26	4.5	131.6	37
Standards	PAAS	"	38.2	79.6	8.83	33.9	5.5	166	"
"	Average Sediments	"	28.3	58.9	6.52	24.9	4.23	122.9	31
"	WMRSS	"	34.5	70.4	8	30	6	148.9	39
"	WARS	"	37.80	77.70	8.77	32.69	6.15	163.1	2

Table 2 shows the average concentrations of La, Ce, Pr, Nd and Sm and Total LREE in Upper Continental Crust (UCC), Post-Archean Australian Shale (PAAS), Average Sediments (AS) and World Major Rivers Suspended Sediments (WMRSS)[31,37,39] respectively for data interpretation and these established standards values were used for present study.

Geo-accumulation index (Igeo): Basically, Igeo was used for assessment contamination level of heavy metal given by Muller[25]. Recently this method adopted to analyze contamination level of REE in sediments, especially for river and marine sediments.

Igeo = Cn/1.5Bn

where Cn is analyzed concentration in river sediments for La, Ce, Pr, Nd and Sm, Bn is background value for element n and factor 1.5 is the possible variations of background value due to lithological variations. For background value of bedload and suspended sediment, we used Average Sediments[31] and World Major Rivers Suspended Sediments[39].

Results and Discussion

La, Ce, Pr, Nd and Sm in Gomati and Sai River: The geochemical analysis of La, Ce, Pr, Nd and Sm in the bedload and the suspended sediments of the Gomati and Sai Rivers are presented in table 3. The total LREE concentration of the bedload and suspended sediments in the Gomati River (Zafrabad) was 76.7 µg/g and 179.4 µg/g respectively. The total LREE concentration of the bedload and suspended sediments in the Sai River (Haripur) was 151.2 µg/g and 229.0 µg/g respectively. The total LREE concentration of the Sai River bedload and suspended sediments are much higher than the concentration of Average Sediments (122.9 µg/g) and Upper Continental Crust (131.6 µg/g). Figure 2(a) displays the bar diagram representing the La, Ce, Pr, Nd and Sm concentration of the suspended sediments higher than the bedload sediments of the Gomati River (Kerakat).

According to Singh et al[34] the coarser sand fractions have lower and the finer silt and clay fractions have higher REE abundance than the bulk sample. It can be concluded that the grain size properties of the river sediments controlled REE distribution in the river basin. The 600 Km long, Sai River is the main tributary of the Gomati River and drains nearly one-third area of the GRB. Figure 3 displays the bar diagrams to understand the Gomati and Sai basin effects on La, Ce, Pr, Nd and Sm concentrations in river sediments. The concentration of these elements in bedload and suspended sediments of the Sai River (229.0 µg/g) was measured higher than the Gomati River (192.3 µg/g). The comparative study indicates that the Sai River Basin is more contaminated with LREE than the GRB because several sugarcane industries located along the river bank like Jarwal, Balha Nanpara, Chilawaria and Kaisharganj, generate large quantity of bagasse and molasses.

Table 3
The concentrations of La, Ce, Pr, Nd and Sm in the bedload and suspended load sediments of the Gomati and Sai Rivers. Refer Fig. 1 for the location of sediments sampling sites.

River	Sampling Location	Sediment type	Light Rare Earth Elements (in µg/g)					∑LREE
			La	Ce	Pr	Nd	Sm	
Gomati River	Zafrabad	Bedload	18.0	36.3	4.1	15.3	3.0	76.7
,,	,,	Suspended Load	42.2	85.2	9.4	35.6	6.9	179.4
Sai River	Haripur	Bedload	35.6	72.1	8.1	29.6	5.8	151.2
,,	,,	Suspended Load	54.0	108.6	12.1	45.5	8.8	229.0
Gomati River	Kerakat	Bedload	33.4	66.7	7.5	27.7	5.3	140.6
,,	,,	Suspended Load	48.5	97.2	11.0	40.4	8.0	205.2

Table 4
La, Ce, Pr, Nd and Sm concentrations (in µg/g) in biotite associated with the mica-rich bedload sediments of the Gomati River[42]. Refer Fig. 1 for sampling locations. The La, Ce, Pr, Nd and Sm data of biotite in the Ganga River bedload sediments is from Garcon[11].

River	Gomati				Ganga Delta
Sampling Location	Naimeserayan	Haidergarh	Sultanpur	Chandwak	Kushtia
Downstream distance.	245 km	476 km	660 km	861 km	2000 km
	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
La	83.4	100.6	142.1	329.4	60.9
Ce	158.8	198.9	284.0	638.9	110
Pr	17.8	21.9	31.2	71.5	10.2
Nd	64.3	79.2	112.2	256.4	32.0
Sm	12.1	14.5	21.1	46.1	4.77
∑LREE	338.7	417.3	594.9	1348.5	217.9

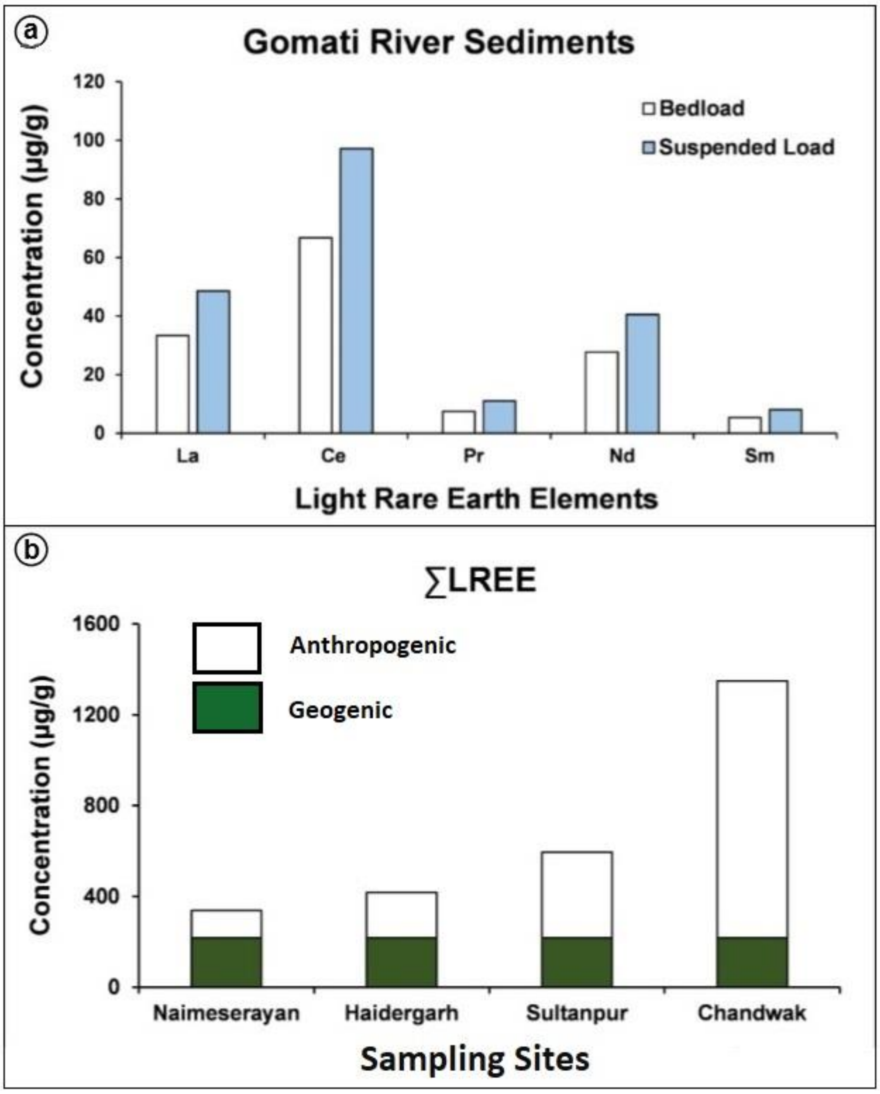

Figure 2: Bar diagrams showing the distribution of Light Rare Earth Elements (in µg/g) in (a) the Gomati River Sediments at Kerakat and (b) Biotite of the mica-rich bedload sediments of the Gomati River. Refer Fig. 1 for the location of Sampling site and Tables 3 and 4 for the LREE data. Note the higher concentration of La, Ce, pr, Nd and Sm in the suspended sediments than the bedload sediments due to effect of grainsize and mineralogy of the Gomati River Sediments. It is important to note that biotite displays the downstream increase of anthropogenic LREE in the GRB. The geogenic contribution of LREE in biotite derived from the Ganga River Sediments is taken from Garcon et al[11].

Bagasse can be utilized in the manufacturing of paper and black board alcohol and sprit can be made from molasses[21]. According to Chua et al[6], Cerium could enter into sugarcane plants via the leaves that were exposed to atmospheric contaminants and REE could also enter into sugarcane plants via the roots in substrate soils that were contaminated by REE or applied with fertilizers containing REEs. The high REE concentrations in the substrate soil on which sugarcane grows, could lead to harmful effects for humans consuming sugarcane-related products.

La, Ce, Pr, Nd and Sm in Biotite: Table 4 presents the La, Ce, Pr, Nd and Sm concentration in Biotite of the mica-rich bedload sediments collected from the Gomati River. The four sampling site namely are Naimeserayan (338.7 µg/g), Haidergarh (417.3 µg/g), Sultanpur (594.9 µg/g) and Chandwak (1348.5 µg/g). The LREE in biotite derived from the Ganga River sediments (217.9 µg/g) as reported by Garcon et al[11] was considered as geogenic fraction to understand the anthropogenic contribution of La, Ce, Pr, Nd and Sm concentration in biotite of the Gomati River Sediments. The downstream increasing trend of anthropogenic LREE content biotite is shown in figure 2(b). This increasing concentration may be responsible for anthropogenic contamination displaying that biotite is a good geogenic indicator, which is sensitive enough to record the LREE contamination in the Gomati River.

Himalayan Region vs. Ganga Alluvial Plain rivers: The Ganga river draining Himalayan region is showing increased concentraion of total LREE 83.0 µg/g [29], 149.1 µg/g [5], 149.2 µg/g [36] and 160.3 µg/g [27] whereas rivers of Ganga Alluvial plain shows 171.2 µg/g [11], 145.9 µg/g [18] and very high concentration were observed in the Gomati River (192.3 µg/g) and Sai River (229.0 µg/g) in suspended sediments in persent study. Figure 4 shows the trend line of increasing concentration from Himalaya to alluvial rivers. According to Ramesh et al[29], Himalayan Rivers shows enrichment of LREE when compared to HREE due to the substantial fractionation that takes place within the weathering profile.

The Gomati and Sai River drain alluvial plain showed the second cycle of weathering. This enrichment of LREE reflects the intense silicate weathering of crustal materials and a resultant increase in LREE in the detrital grains but when these rivers enters in alluvial plain and highly industrial urban center, lots of anthropogenic activity take place that increase concentrations of these elements in environmental components such as groundwater, lake and river and interact with them. Table 2 shows the concentration of La, Ce, Pr, Nd, Sm and total LREE in Bedload and Suspended sediment of rivers draining Himalyan and alluvial plain along with global standard values.

La, Ce, Pr, Nd and Sm in Hindon River Sediment: In order to characterise the anthropogenic imprints La, Ce, Pr, Nd and Sm in the suspended sediments collected from the 15 sampling sites along the Hindon River (Supplementary table A2). The LREE concentrations in the suspended sediments displayed a wide range for La (49–335 µg/g), Ce (99–866 µg/g), Pr (10–76 µg/g), Nd (42–208 µg/g) and Sm (8–51 µg/g). Figure 5(a) displays the downstream variation in the total LREE content in the suspended sediments ranging from 208 µg/g to 1519 µg/g with two distinct peaks at Greater Noida and Ghaziabad urban sites.

For the understanding of the anthropogenic imprints in the LREE distribution of the Hindon River, all values are normalized with the World Average River Silt. The WARS-normalized pattern is displayed in fig. 5(b), indicating the flat pattern with progressive LREE enrichment. The Hindon River is classified as a LREE contaminated river of the Gangetic Plain.

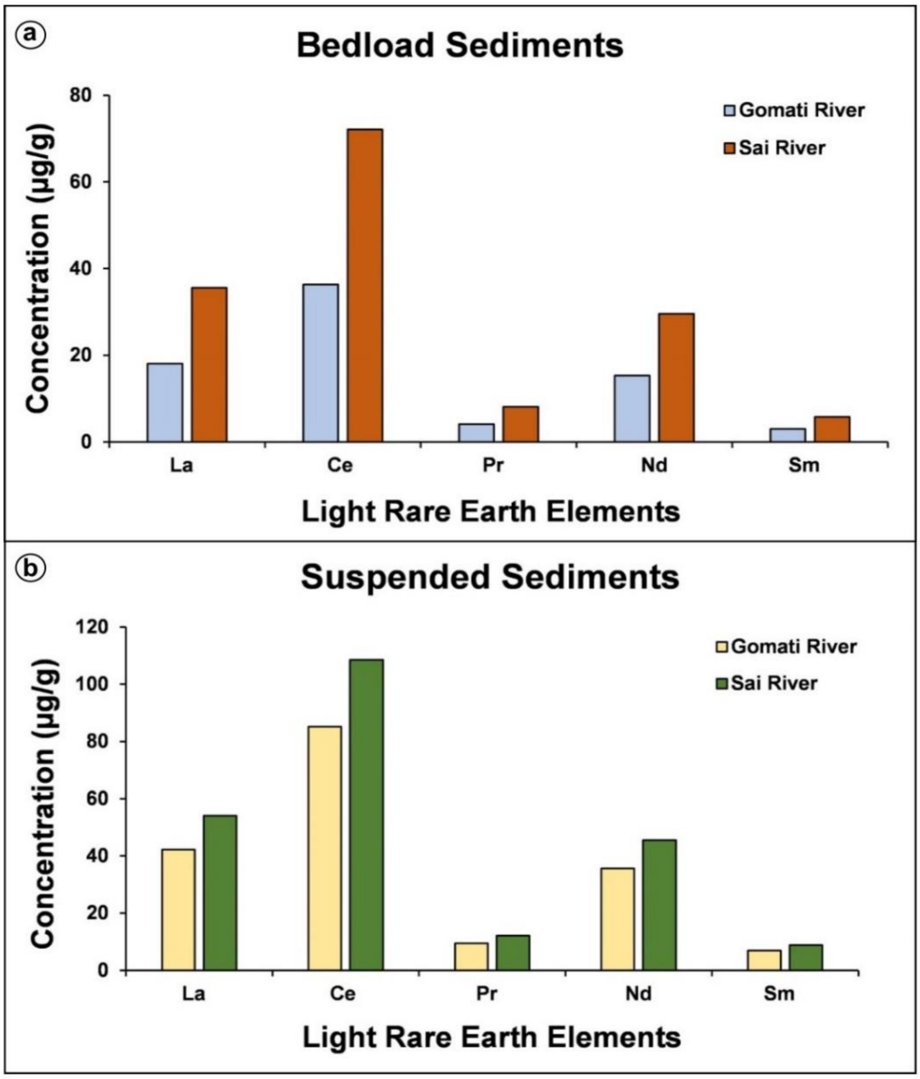

Figure 3: Bar diagram showing the La, Ce, Nd and Sm (in µg/g) concentration in (a) the bedload and (b) the suspended load sediments of the Gomati River (Zafrabad) and the Sai River (Haripur)

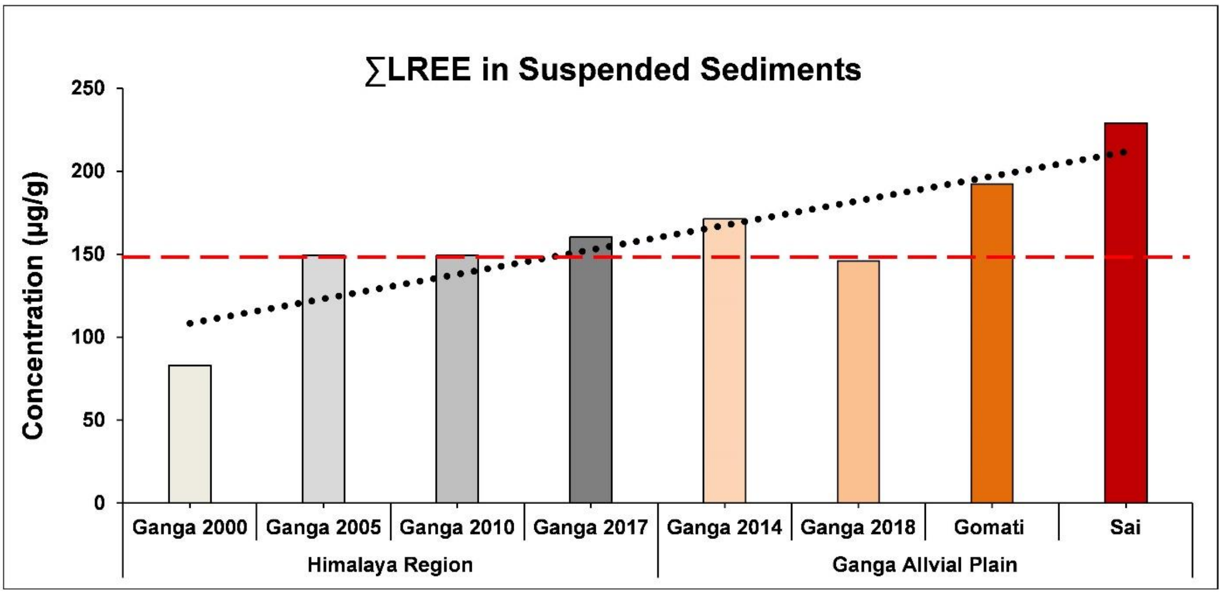

Figure 4: Bar diagrams showing concentration of Total LREE in the suspended sediments of the rivers draining Himalayan region, Ganga Alluvial Plain and Present study. The trend line showing increasing trend towards Gomati and Sai rivers. [Data sources: Ganga 2000[29], Ganga 2005[5], Ganga 2010[36], Ganga 2017[27], (Himalayan Region), Ganga 2014[11], Ganga 2018[18] and Gomati and Sai River of Present study (Ganga Alluvial Plain)].
Note: Red Dashed line shows World Major Rivers Suspended Sediments as geogenic value.

Supplementary Table A2
The concentrations of La, Ce, Pr, Nd and Sm in the suspended load sediments of the Hindon River (A tributary of the Yamuna River). Bold samples S38 and S42 were from High-tech townships in Greater Noida and Ghaziabad as in fig. 1[23].

Sampling Location	Light Rare Earth Element (in µg/g)					∑LREE
	La	Ce	Pr	Nd	Sm	
S3	77	153	16	64	12	322
S7	67	135	14	57	11	284
S12	63	128	13	53	10	267
S15	67	134	14	56	11	282
S17	49	99	10	42	8	208
S21	131	258	27	112	21	549
S22	83	165	17	70	13	348
S34	89	179	19	76	14	377
S37	73	146	15	62	12	308
S38	**325**	**866**	**69**	**208**	**51**	**1519**
S39	129	261	31	120	19	560
S40	85	159	14	60	15	333
S41	92	182	16	70	16	376
S42	69	150	13	66	15	313
S43	**335**	**722**	**76**	**198**	**46**	**1377**

Enrichment Factor (EF): The LREE concentrations in the suspended sediments of World Major Rivers Suspended Sediments (WMRSS) given by Viers et al[39] can be considered the standard for uncontaminated suspended sediments shown in table 2. The LREE enrichment factor was calculated by comparing the LREE values with the World's WMRSS. Figure 6 displays the enrichment factor of LREE contamination in the suspended sediments of the Ganga River draining the Himalayan region and the Gomati, Sai and Hindon Rivers draining the Gangetic Plain. The LREE enrichment factor in the river sediments of the Gangetic Plain displayed the range of one order of magnitude, indicating the high-technology based diversity of anthropogenic imprints on the river basins.

Geo-accumulation index (Igeo): The Igeo has been broadly applied in European trace metal studies since the late 1960s[25] but recently this method has been used very frequently for assessment contamination level of REE[19,42]. All the samples of Gomati River Bedload (BL) and Suspended Sediment (SS) shows (Igeo 0-1)- unpolluted to moderately polluted nature. Sai River BL and SS shows (Igeo 0-1) unpolluted to moderately polluted and (Igeo 1-2) moderately polluted nature respectively. In Hindon River, sampling location Ghaziabad and Greater Noida clearly indicated (Igeo>5) extremely polluted because of highly industrial area in these urban centers situated along the river bank. Sampling site S39 shows (Igeo 2-3) moderately to strongly polluted and other sites S3, S7, S12, S15, S22, S34, S37, S40, S41 and 42 represent (Igeo 1-2) moderately polluted sediment quality (Table 5). The general trend contamination of Igeo was Ce>Pr>La>Sm>Nd in Hindon river suspended sediments.

Conclusion

In the present day, increasing demands and disposal of La, Ce, Pr, Nd and Sm (LREE) raise the concentration in our environmental components that provide us an opportunity to study the modern micro-emerging containment in river system. The river sediments and high technology based anthropogenic activities have controlling influence of accumulation and transportation of anthropogenically originated these elements in rivers of the Gangetic Plain. The LREE concentration in finer fraction (suspended load) is higher than coarser fraction (Bedload) in Gomati and Sai River.

The increasing downstream concentration of LREE in Biotite is identified as an anthropogenic release of contaminants in the GRB. The decadal increase of LREE concentration at Ganga River (Rishikesh) indicates the anthropogenic input of these elements. The Hindon River Basin can act as a natural laboratory to evaluate the impact of LREE contamination on the river's environmental health.

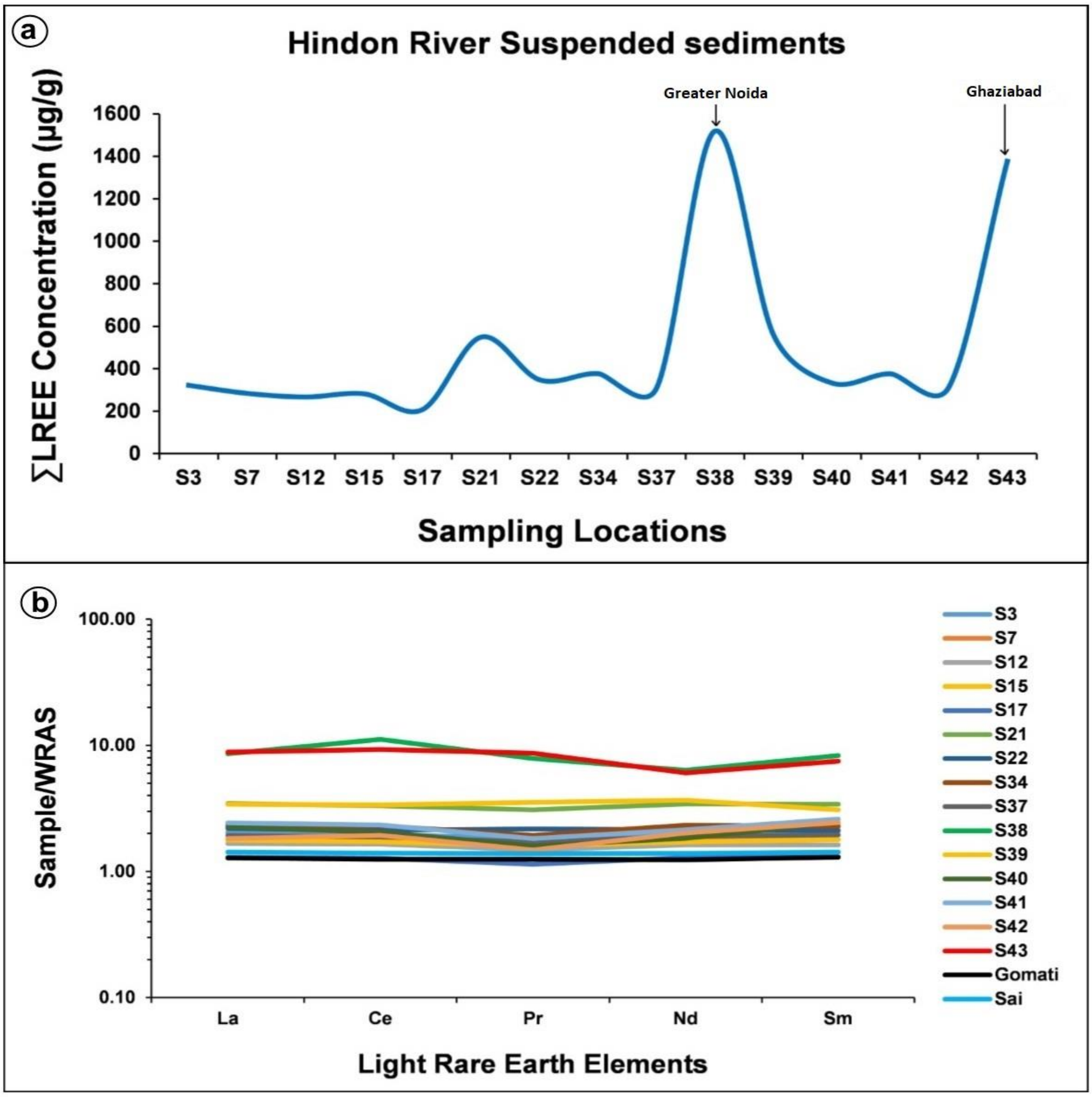

Figure 5: The Hindon River's suspended sediments: (a) line diagram showing downstream variation in concentrations the total Light Rare Earth Elements and (b) the WRAS-normalized pattern of. Refer fig. 1 for location and Supplementary Table A2 for data. Note the peaked LREE contamination level was represented by the sediment samples of Greater Noida (S38) and Ghaziabad (S43) locations[23]

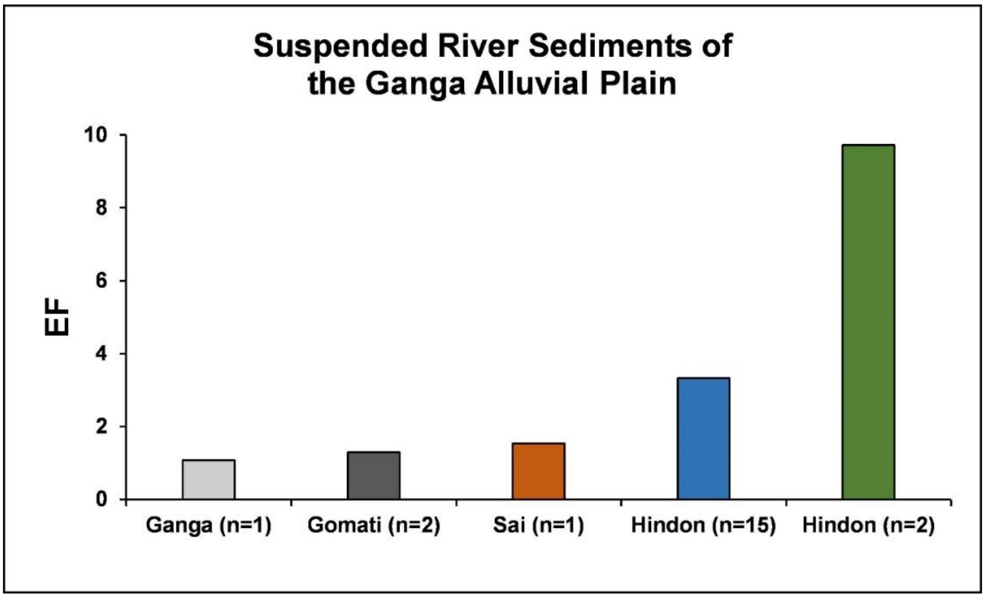

Figure 6: Bar diagram showing the enrichment factor (EF) of LREE contamination in the suspended sediments of the Ganga River draining the Himalayan region and the Sai, the Gomati and the Hindon Rivers draining the Ganga Alluvial Plain. The LREE concentrations in the World Major Rivers Suspended Sediments given by Viers et al[39] is considered as a reference for uncontaminated suspended river sediments and used for the calculation of the enrichment factor.

Table 5
(Upper) Data of Geo-accumulation Index (Igeo) in Bedload (BL) and Suspended load (SS) of Gomati, Sai and Hindon Rivers of Gangetic Plain. (Note: DNA= Data Not Available) and (Lower) table represent Contamination scale[25].

Geo-accumulation Index (Igeo)											
Rivers	Sampling Location/Code	La		Ce		Pr		Nd		Sm	
		BL	SS	BL	SS	BL	SS	BL	SS	BL	SS
Gomati	Zafrabad	0.42	0.82	0.41	0.81	0.42	0.79	0.41	0.79	0.47	0.77
Gomati	Kerakat	0.79	0.94	0.76	0.92	0.76	0.91	0.74	0.90	0.84	0.89
Sai	Haripur	0.84	1.04	0.82	1.03	0.83	1.01	0.79	1.01	0.91	0.98
Hindon	S3	DNA	1.49	DNA	1.45	DNA	1.33	DNA	1.42	DNA	1.33
	S7	"	1.29	"	1.28	"	1.17	"	1.27	"	1.22
	S12	"	1.22	"	1.21	"	1.08	"	1.18	"	1.11
	S15	"	1.29	"	1.27	"	1.17	"	1.24	"	1.22
	S17	"	0.95	"	0.94	"	0.83	"	0.93	"	0.89
	S21	"	2.53	"	2.44	"	2.25	"	2.49	"	2.33
	S22	"	1.60	"	1.56	"	1.42	"	1.56	"	1.44
	S34	"	1.72	"	1.70	"	1.58	"	1.69	"	1.56
	S37	"	1.41	"	1.38	"	1.25	"	1.38	"	1.33
	Greater Noida	"	6.28	"	8.20	"	5.75	"	4.62	"	5.67
	S39	"	2.49	"	2.47	"	2.58	"	2.67	"	2.11
	S40	"	1.64	"	1.51	"	1.17	"	1.33	"	1.67
	S41	"	1.78	"	1.72	"	1.33	"	1.56	"	1.78
	S42	"	1.33	"	1.42	"	1.08	"	1.47	"	1.67
	Ghazibad	"	6.47	"	6.84	"	6.33	"	4.40	"	5.11

I	Igeo>5	Extremely Polluted
II	Igeo 4-5	Strongly to Extremely Polluted
III	Igeo 3-4	Strongly Polluted
IV	Igeo 2-3	Moderately to Strongly Polluted
V	Igeo 1-2	Moderately Polluted
VI	Igeo 0-1	Unpolluted to Moderately Polluted
VII	Igeo < 0	Practically unpolluted

The LREE enrichment factor in the river sediments is showing the one order magnitude. The Geo-accumulation index (Igeo) shows that some sampling sites (Ghaziabad and Greater Noida) of Hindon River are at high risk of extremely contaminated zone. These elements show toxicity in suspended sediments of Hindon river in decreasing in order to Ce>Pr>La>Sm>Nd. Additionally, studies on the toxicological effects of these elements may soon be able to forecast how these elements surroundings may affect human health in the future.

Acknowledgement

Author is thankful to Head, Department of Geology, University of Lucknow, for providing the necessary facilities for the completion of this work and to Prof. M. Singh for his valuable suggestions and constructive comments during the preparation of the manuscript.

References

1. Aubert D., Stille P., Probst A., Gauthier-Lafaye F., Pourcelot L. and Nero M.D., Characterisation and migration of atmospheric REE in soils and surface waters, *Geochim. Cosmochim. Acta*, **66(19)**, 3339-3350, https://doi:10.1016/S0016-7037(02)00913-4 **(2002)**

2. Bayon G., Toucanne S., Skonieczny C., Andre L., Bermell S., Cheron S. and Barrat J.A., Rare earth elements and neodymium isotopes in world river sediments revisited, *Geochim. Cosmochim. Acta*, **170**, 17-38, https://doi:10.1016/j.gca.2015.08.001 **(2015)**

3. Blinova I., Lukjanova A., Muna M., Vija H. and Kahru A., Evaluation of the potential hazard of lanthanides to freshwater microcrustaceans, *Sci. Total Environ*., **642**, 1100-1107, https://doi:10.1016/j.scitotenv.2018.06.155 **(2018)**

4. Censi P., Sposito F., Inguaggiato C., Zuddas P., Inguaggiato S. and Venturi M., Zr, Hf and REE distribution in river water under different ionic strength conditions, *Sci. Total Environ*., **645**, 837-853, https://doi:10.1016/j.scitotenv.2018.07.081 **(2018)**

5. Chakrapani G.J., Major and trace element geochemistry in upper Ganga River in the Himalayas, India, *Environ. Geol.*, **48(2)**, 189-201, https://doi:10.1007/s00254-005-1287-1 **(2005)**

6. Chua H., Zhao Y.G., Kwang Y.H., Liu Q.Y. and Liu X.H., Accumulation of environmental residues of rare earth elements in sugarcane, *Environ. Int*., **24(3)**, https://doi:10.1016/s0160-4120(98)00007-5 **(1998)**

7. Cuss C.W., Donner M.W., Grant-Weaver I., Noernberg T., Pelletier R., Sinnatamby R.N. and Shotyk W., Measuring the distribution of trace elements amongst dissolved colloidal species as a fingerprint for the contribution of tributaries to large boreal rivers, *Sci. Total Environ*., **642**, 1242-1251, https://doi:10.1016/j.scitotenv.2018.06.099 **(2018)**

8. Ding S., Liang T., Zhang C., Huang Z., Xie Y. and Chen T., Fractionation mechanisms of rare earth elements (REEs) in hydroponic wheat: an application for metal accumulation by plants, *Environ. Sci. Technol*., **40(8)**, 2686-2691, https://doi:10.1021/es052091b **(2006)**

9. Forstner U. and Wittmann G.T., Metal Pollution in Aquatic Environment, 2nd Edition, Springer-Verlag, Berlin, https://doi:10.1007/978-3-642-69385-4 **(1981)**

10. Gaman L., Radoi M.P., Delia C.E., Luzardo O.P., Zumbado M., Rodríguez-Hernández Á., Stoian I., Gilca M., Boada L.D. and Henríquez-Hernández L.A., Concentration of heavy metals and rare earth elements in patients with brain tumours: Analysis in tumour tissue, non-tumour tissue and blood, *Int. J. Environ. Health Res*., **31**, 741-754, https://doi:10.1080/09603123.2019.1685079 **(2021)**

11. Garcon M. and Chauvel C., Where is basalt in river sediments and why does it matter?, *Earth Planet. Sci. Lett.*, **407**, 61-69, https://doi:10.1016/j.epsl.2014.09.033 **(2014)**

12. Gwenzi W., Mangori L., Danha C., Chaukura N., Dunjana N. and Sanganyado E., Sources, behaviour and environmental and human health risks of high-technology rare earth elements as emerging contaminants, *Sci. Total Environ*., **636**, 299-313, https://doi:10.1016/j.scitotenv.2018.04.235 **(2018)**

13. Hissler C., Hostache R., Iffly J.F., Pfister L. and Stille P., Anthropogenic rare earth element fluxes into floodplains: coupling between geochemical monitoring and hydrodynamic sediment transport modelling, *C. R. - Geosci.*, **347(5-6)**, 294-303, https://doi:10.1016/j.crte.2015.01.003 **(2015)**

14. Kulaksız S. and Bau M., Rare earth elements in the Rhine River, Germany: First case of anthropogenic lanthanum as a dissolved micro contaminant in the hydrosphere, *Environ. Int*., **37(5)**, 973-979, https://doi:10.1016/j.envint.2011.02.018 **(2011)**

15. Kumar S. and Singh I.B., Sedimentological Study of Gomati River Sediments, Uttar Pradesh, India. Example of a river in Alluvial Plain, *Senckenbergiana Maritima*, **10(4-6)**, 145-211 **(1978)**

16. Langmuir D., Aqueous Environmental Geochemistry, Prentice-Hall, Inc., Englewood Cliffs, 601 **(1997)**

17. Li Z., Liang T., Li K. and Wang P., Exposure of children to light rare earth elements through ingestion of various size fractions of road dust in REEs mining areas, *Sci. Total Environ*., **15(743)**, 140432, https://doi:10.1016/j.scitotenv.2020.140432 **(2020)**

18. Maharana C., Srivastava D. and Tripathi J.K., Geochemistry of sediments of the Peninsular Rivers of the Ganga basin and its implication to weathering, sedimentary processes and provenance, *Chem. Geol.*, **483**, 1-20, https://doi:10.1016/j.chemgeo.2018.02.019 **(2018)**

19. Mejjad N., Laissaoui A., Benmhammed A., Fekri A., Hammoumi O. El., Benkdad H., Amsil H. and Chakir El. M., Potential ecological risk assessment of rare earth elements in sediments cores from the Oualidia lagoon, Morocco, *Soil Sediment Contam.*, **31(8)**, 941-58, https://doi:10.1080/15320383.2022.2027342 **(2022)**

20. Migaszewski Z.M. and Gałuszka A., The Characteristics, Occurrence and Geochemical Behavior of Rare Earth Elements in the Environment: A Review Critical Reviews, *Environ. Sci. Technol*., **45(5)**, 429-471, https://doi:10.1080/10643389.2013.866622 **(2015)**

21. Ministry of MSME, District Industrial Profile of Bahraich district, MSME- Development Institute, Allahabad, Government of India **(2024)**

22. Mishra S., Kumar A. and Shukla P., Study of water quality in Hindon River using pollution index and environmetrics, India, *Desalin Water Treat*, **57(41)**, 19121-19130, https://doi:10.1080/19443994.2015.1098570 **(2015)**

23. Mondal M.E.A., Wani H. and Mondal B., Geochemical signature of provenance, tectonics and chemical weathering in the Quaternary flood plain sediments of the Hindon River, Gangetic plain, India, *Tectonophysics*, **566-567**, 87-94, https://doi:10.1016/j.tecto.2012.07.001 **(2012)**

24. Morin-Crini N., Lichtfouse E., Liu G., Balaram V., Ribeiro A.R.L., Lu Z., Stock F., Camona M.R.T., Picos-Carrales L.A., Moreno-Pirajan J.C., Giraldo L., Li C., Pandey A., Hocquet D., Torri G. and Crini G., Emerging Contaminants: Analysis, Aquatic Compartments and Water Pollution, *Emerging Contaminants*, https://doi:10.1007/978-3-030-69079-3_1 **(2021)**

25. Müller G., Schwermetalle in den Sedimenten des Rheins-Veranderungenseit 1971, *Umschau*, **79(24)**, 778-783 **(1979)**

26. Nriagu J.O. and Pacyna J.M., Quantitative assessment of worldwide contamination of air, water and soils by trace metals, *Nat*., **333**, 134-139, https://doi:10.1038/333134a0 **(1988)**

27. Panwar S., Khan M.Y.A. and Chakrapani G.J., Grain size charcterstics and provenance determination of sediments and dissolved load of Alaknanda River, Garhwal Himalaya, India, *Environ. Earth Sci*., https://doi:10.1007/s12665-015-4785-9 **(2027)**

28. Ramachandran R., Urbanisation and Urban systems in India, Oxford University Press, Delhi, 364 **(1989)**

29. Ramesh R., Ramanathan A., Ramesh S., Purvaja R. and Subramanian V., Distribution of rare earth elements and heavy metals in the surficial sediments of the Himalayan river system, *Geochem. J*., **34**, 295-319, https://doi:10.2343/geochemj.34.295 **(2000)**

30. Rollinson H., Using geochemical data, Evaluation, Presentation, Interpretation, Harlow, Longman Scientific & Technical, Harlow, UK, 352 **(1993)**

31. Ronov A.B., The Earth's Sedimentary Shell Quantitative Patterns of its Structure, Composition and Evolution, by A.B., AC1 Reprint Series, 80 **(1983)**

32. Silva Y.J.A., Bezerra D.N., Clístenes W.A., da Silva Y.J.A., Bezerra A., Fábio F.C., José R.B., Singh V.P. and Collins A.L., Bed and suspended sediment-associated rare earth element concentrations and fluxes in a polluted Brazilian river system, *Environ. Sci. Pollut. Res*., https://doi:10.1007/s11356-018-3357-4 **(2018)**

33. Singh I.B., Geological Evolution of Ganga Plain- an overview, *J Palaeontol Soc Ind*., **41**, 99-137 **(1996)**

34. Singh P. and Rajamani V., REE geochemistry of recent clastic sediments from the Kaveri flood plains, South India: implications to source area weathering and sedimentary processes, *Geochimica et Cosmochimica Acta*, **65(18)**, 3093-3108, https://doi:10.1016/S0016-7037(01)00636-6 **(2001)**

35. Singh P., Major, trace and REE geochemistry of the Ganga River sediments: Influence of provenance and sedimentary processes, *Chem. Geol.*, **266**, 242-255, https://doi:10.1016/j.chemgeo.2009.06.013 **(2009)**

36. Singh P., Geochemistry and provenance of stream sediments of the Ganga River and its major tributaries in the Himalayan region, India, *Chem. Geol.*, **269(3-4)**, 220-36, https://doi:10.1016/j.chemgeo. 2009.09.020 **(2010)**

37. Taylor S.R. and McLennan S.M., The continental crust: its composition and evolution, Blackwell Scientific Publication, Oxford **(1985)**

38. UNESCO, A global geochemical database for environmental and resource management, Earth Science, 19, UNESCO Publication, Paris **(1995)**

39. Viers J., Dupré B. and Gaillardet J., Chemical composition of suspended sediments in World Rivers: New insights from a new database, *Sci. Total Environ*., **407(2)**, 853-868, https://doi:10.1016/j.scitotenv.2008.09.053 **(2009)**

40. Wei J., Wang C., Yin S., Pi X., Jin L. and Li Z., Concentrations of rare earth elements in maternal serum during pregnancy and risk for fetal neural tube defects, *Environ. Int*., **137**, 105542, https://doi.org/10.1016/j.envint.2020.105542 **(2020)**

41. Xu N., Morgan B. and Rate A.W., From source to sink: rare-earth elements trace the legacy of sulfuric dredge spoils on estuarine sediments, *Sci. Total Environ*., **637-638**, 1537-1549, https://doi:10.1016/j.scitotenv.2018.04.398 **(2018)**

42. Yadav J.K., Singh P., Kidwai A., Kumar N., Singh S., Singh S., Kar R. and Singh M., Light Rare Earth Elements in Freshly Deposited River Sediments of Ganga Alluvial Plain, northern India: Geogenic variability and Anthropogenic influences, *Soil Sediment Contam*, https://doi.org/10.1080/15320383.2024.2384920 **(2024)**

43. Zhang H., Feng J., Zhu W., Liu C., Wu D., Yang W. and Gu J., Rare earth element distribution characteristics of biological chains in rare-earth element-high background regions and their implications, *Biol. Trace Elem. Res*., **73(1)**, 19-27, https://doi:10.1385/bter:73:1:19 **(2000)**

44. Zheng L., Zhang J., Yu S., Ding Z., Song H., Wang Y. and Li Y., Lanthanum Chloride Causes Neurotoxicity in Rats by Up regulating miR-124 Expression and Targeting PIK3CA to Regulate the PI3K/Akt Signaling Pathway, *Biomed Res. Int*., **5**, 5205142, https://doi:10.1155/2020/5205142 **(2020)**.

(Received 09th November 2024, accepted 08th January 2025)