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Geochemistry of Rare Earth Elements in Sediment of Central India

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Abstract

The rare earth elements (REE) are of great interests due to wide industrial applications. In the present work, geochemistry of REE in the contaminated pond sediment of Ambagarh Chowki, central India is described. The concentration (n = 24) of La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and U was ranged from 16 - 119, 41 - 163, 4.1 - 28, 16 - 99, 0.7 - 2.7, 3.2 - 18, 2.7 - 16, 0.4 - 2.3, 2.2 - 13, 0.4 - 2.4, 1.1 - 6.1, 0.2 - 0.8, 0.9 - 4.8, 0.13 - 0.70, 6 - 25 and 0.46 - 1.86 mg/kg with mean value of 42 ± 9, 89 ± 13, 9.4 ± 1.9, 34 ± 7, 1.2 ± 0.2, 6.3 ± 1.2, 5.4 ± 1.0, 0.8 ± 0.1, 4.2 ± 0.8, 0.8 ± 0.2, 2.0 ± 0.4, 0.3 ± 0.1, 1.6 ± 0.3, 0.24 ± 0.04, 11 ± 2 and 1.14 ± 0.13 mg/kg, respectively. The concentration ratio of ∑LREE/∑HREE, La/Y and Th/U are discussed. The spatial distribution and sources of the REE are described.

Keywords

Rare Earth Element, Sediment, Geochemistry, Sources

1. Introduction

The rare earth elements (REE) including actinide have wide industrial applications in several fields *i.e.* nuclear energy as fuel and modifier, organic synthesis as catalyst, ceramics as coloring agents, X-ray tubes as phosphors, etc. [1] [2]. The distribution of REE in various environmental materials *i.e.* soil and sediments was reported [3]-[13]. Recently, the health hazards of the REE were highlighted [14] [15]. The environment of the Ambagarh Chowki block, central India is seriously contaminated with As and heavy metals [16]. In this work, the geochemistry of the REE in pond sediments of Ambagarh Chowki block, Rajnandgaon district, central India is described.

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2. Materials and Methods

2.1. Study Area

Arsenic and other heavy metals are deposited in the environment of Ambagarh Chowki block, Rajnandgaon district, Chhattisgarh, India over area ≈3000 km^{-2}. The Ambagarh Chowki block falls in a tribal belt with population of ≈0.1 million. This block covers 155 villages and towns which suffering with serious health hazards due to contamination of the environment with toxic elements. In this work, 24 ponds lie in different 11 villages (locations) of Ambagarh Chowki block were selected for the investigation of the REE contamination (**Figure 1**).

2.2. Sampling

The composite surface sediment sample (0 - 10 cm) was collected from five points in the equal ratio from each pond as prescribed in literature [17]. For the depth profile studies, the samples at the depth profile of 0 - 10, 10 - 20 and 20 - 30 cm of the Bhadsena pond was collected.

2.3. Analysis

The samples were dried, crushed and sieved out the particles of size ≤ 1 mm. A 0.25 g of each sediment sample was digested with 8 ml aqua regia in the closed microwave vessel for 15 min. An aliquot of the extract was diluted with deionized water for the further analysis. The *Thermo Fisher* ICP-OES and ICP-MS (Polish Geological Institute, NRI, Central Chemical Laboratory, and Warsaw) were employed for analysis of the elements. The NCS DC 73382 CRM sediment sample was used for the quality control. The background levels of the REE reported in the upper earth crust were used for computation of the enrichment factor (E_f) by using following equation [18].

$$E_f = \{[X_s]/[Al_s]\} / \{[X_e]/[Al_e]\}$$

where, X_s, Al_s, X_e and Al_e are concentrations of metal and Al in the soil and earth crust, respectively.

3. Results and Discussion

The sediment was found to be colored from light brown (LBr) to dark brown (DBr), **Table 1**. The pH value of the extract was ranged from 6.5 - 8.1 with mean value of 7.2 ± 0.2.

3.1. Concentration of Elements

The concentrations of 49 elements in 24 pond sediments are shown in **Tables 1-4**. The concentration of elements *i.e.* Fe, Al, Ca, Mg, K, Mn, Ti, Na, P, S, Ba, V, Zn, Cu, As, Ni, Cr, Co, Sr, Pb, Rb, Ga, Li, Be, Mo, Ag, Cd, Sn, Sb, Cs, Bi, Th, U, Sc, Y, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Tb and Lu was ranged from 25,400 - 65,900, 11,800 - 34,700, 1500 - 16,100, 1500 - 30,200, 1200 - 4500, 256 - 1660, 62 - 735, 90 - 830, 90 - 570, 50 - 790, 88 - 304, 29 - 166, 32 - 100, 28 - 89, 10 - 53, 19 - 340, 24 - 1298, 9 - 76, 10 - 69, 10 - 40, 12 - 46, 7 - 15, 5 - 18, 0.9 - 3.4,0.14 - 1.32, 0.07 - 2.36, 0.05 - 0.39, 0.8 - 2.6, 0.27 - 0.97, 0.5 - 2.2, 0.10 - 0.30, 6.1 - 25, 0.5 - 1.9, 3.0 - 25, 11 - 61, 16 - 119, 41 - 163, 4.0 - 28, 16 - 99, 0.7 - 2.7, 3.2 - 18, 2.7 - 16, 0.4 - 2.3, 2.2 - 13, 0.4 - 2.4, 1.1 - 6.1, 0.15 - 0.83, 0.9 - 4.8 and 0.13 - 0.70 mg/kg with mean value of 44842 ± 5133, 23813 ± 2819, 5133 ± 1418, 6850 ± 2581, 2708 ± 243, 759 ± 158, 254 ± 79, 355 ± 93, 268 ± 45, 285 ± 81, 196 ± 21, 84 ± 16, 63 ± 7, 52 ± 6, 22 ± 5, 75 ± 30, 177 ± 118, 30 ± 7, 26 ± 6, 23 ± 3, 26 ± 3, 11 ± 1, 12 ± 2, 1.6 ± 0.2, 0.63 ± 0.14, 0.67 ± 0.23, 0.13 ± 0.03, 1.5 ± 0.2, 0.44 ± 0.05, 1.2 ± 0.2, 0.15 ± 0.03, 11 ± 2, 1.1 ± 0.1, 11 ± 2, 20 ± 4, 42 ± 8, 42 ± 8, 89 ± 13, 9 ± 2, 34 ± 7, 1.2 ± 0.2, 6.3 ± 1.2, 5.4 ± 1.0, 0.77 ± 0.15, 4.2 ± 0.8, 0.8 ± 0.2, 2.0 ± 0.4, 0.27 ± 0.05, 1.6 ± 0.3 and 0.24 ± 0.04 mg/kg, respectively. Among them, the highest concentration of Fe was marked. They occurred in following decreasing order in the sediment: Fe < Al < Mg < Ca < K < Mn < Na < S < P < Ti < Ba < Ce < Cr < V < Ni < Zn < Cu < La < < Nd < Co < Sr ≈ Rb < Pb < As < Y < Li < Ga ≈ Th ≈ Sc < Pr < Sm < Gd < Dy < Er < Yb ≈ Be < Sn < Eu ≈ Cs < U < Tb ≈ Ho < Ag < Mo < Sb < Tm < Lu < Cd ≈ Bi.

3.2. Concentration of REE

The concentration of the LREE (*i.e.* La, Ce, Pr, Nd, Eu and Sm) and HREE (*i.e.* Gd, Tb, Dy, Ho, Er, Tm, Yb

Table 1. Concentration of major element in sediments, mg/kg.

S. No.	Pond location	Color	Fe	Al	Ca	Mg	K	Mn	Ti	Na
1	Murethitola-1	LBr	62,700	31,400	5800	6300	2900	778	735	160
2	Murethitola-2	LBr	64,900	34,700	7100	6800	3000	956	586	540
3	Murethitola-3	RBr	32,700	17,200	1800	1700	2100	447	166	90
4	Netamtola-1	DB	54,700	32,200	9400	14,300	2500	892	394	630
5	Netamtola-2	B	48,000	32,200	12,500	9200	4000	1474	140	830
6	Netamtola-3	LB	53,800	30,000	16,100	9300	1300	959	455	740
7	Kaudikasa-1	DBr	49,800	30,600	7600	10,800	4000	1109	264	490
8	Kaudikasa-2	RBr	49,500	19,200	2000	2800	4500	467	254	180
9	Kaudikasa-3	LB	25,400	19,200	4700	4800	2400	256	64	220
10	Ghorda-1	Br	45,600	29,400	3700	7700	2900	1660	173	130
11	Ghorda-2	LB	41,000	28,600	5800	30,200	1600	1148	556	100
12	Ghorda-3	LBr	57,700	34,300	7600	17,900	1200	671	571	150
13	Metepar-1	Br	43,600	26,700	4800	6600	2000	856	105	110
14	Metepar-2	LBr	59,000	23,400	3400	4900	2200	878	313	730
15	Metepar-3	LBr	65,900	25,100	3600	5000	2900	540	320	270
16	Bhadsena	LBr	38,000	21,500	2100	2500	3000	350	68	340
17	Sonsaitola-1	LB	28,000	18,600	4800	3700	3200	694	62	280
18	Sonsaitola-2	LBr	28,000	14,100	2500	1800	3400	388	92	330
19	Sonsaitola-3	DBr	32,500	14,800	2500	2200	3800	435	98	600
20	Meregaon	Br	50,000	19,600	3100	2500	2200	1393	185	250
21	Joratarai	DBr	53,100	23,600	3300	5100	2700	853	133	360
22	Thailitola-1	LBr	26,900	11,800	2500	2600	2500	285	125	230
23	Thailitola-2	RBr	33,500	14,700	1500	1500	1700	369	163	140
24	Jadutola	LB	31,900	18,600	5000	4200	3000	350	73	630

Table 2. Chemical characteristics of metal in pond sediment, mg/kg.

S. No.	P	S	Ba	V	Zn	Cu	As	Ni	Cr	Co	Sr	Pb
1	300	80	217	144	76	64	40	51	45	30	29	17
2	380	380	259	160	88	71	17	58	64	44	39	24
3	160	70	129	59	42	53	33	29	39	13	12	20
4	430	790	179	86	90	89	16	133	301	41	42	24
5	420	540	304	87	80	71	12	85	136	39	54	22
6	170	70	150	166	53	49	12	43	56	33	69	12
7	340	600	264	96	88	73	20	108	232	42	30	27
8	320	320	212	48	100	48	53	30	61	18	16	40
9	220	400	179	50	50	41	15	55	120	18	21	23

Continued

10	160	360	300	79	52	47	12	196	635	76	17	39
11	570	90	218	67	54	36	10	340	1298	62	26	22
12	330	110	161	93	65	63	15	194	658	30	28	10
13	200	70	222	95	53	46	19	51	51	28	35	19
14	170	190	204	142	60	56	17	48	45	38	27	15
15	180	180	211	152	68	56	18	49	45	26	27	13
16	330	310	188	55	65	37	12	31	33	13	13	32
17	220	300	213	50	40	35	28	38	50	20	25	19
18	290	470	140	38	54	37	28	23	29	12	12	22
19	220	370	154	47	44	53	30	28	30	14	14	17
20	170	50	221	77	45	42	11	37	47	34	18	27
21	340	300	209	98	87	59	25	77	133	36	22	31
22	150	180	118	29	48	28	34	22	24	11	10	23
23	90	60	88	48	32	32	45	19	30	9	10	24
24	280	550	165	52	67	50	11	49	82	25	21	37

Table 3. Chemical characteristics of minor element in pond sediment, mg/kg.

S. No.	Rb	Ga	Li	Be	Mo	Ag	Cd	Sn	Sb	Cs	Bi	Th	U
1	32	14	14	1.57	0.67	0.15	0.12	1.4	0.46	2.18	0.3	13.2	1.64
2	23	15	13	1.35	0.40	0.69	0.26	1.4	0.35	1.41	0.1	7.2	0.77
3	27	8	8	1.47	0.85	0.13	0.05	1.4	0.43	0.98	0.3	15.7	1.36
4	12	11	17	1.16	0.27	0.73	0.39	1.2	0.51	0.52	0.1	6.1	0.65
5	22	12	14	1.98	0.40	0.92	0.19	2.1	0.4	0.95	0.1	10.2	1.36
6	15	10	11	1.06	0.24	0.07	0.05	1.1	0.42	1.00	0.1	6.5	1.01
7	29	12	17	1.55	0.52	1.60	0.21	1.7	0.52	1.23	0.1	8.0	1.14
8	46	11	9	1.68	1.32	0.16	0.11	1.3	0.59	1.63	0.2	9.3	1.12
9	20	7	9	1.29	0.26	1.70	0.16	1.5	0.27	0.97	0.1	10.1	1.04
10	39	13	18	2.55	0.92	0.56	0.14	2.6	0.50	2.09	0.1	14.1	1.42
11	15	9	18	0.86	0.18	0.26	0.06	1.0	0.35	1.19	0.1	7.6	0.74
12	14	12	15	1.39	0.14	0.19	0.05	2.0	0.3	1.08	0.1	8.0	0.46
13	28	10	14	1.47	0.20	0.13	0.06	1.3	0.34	1.69	0.1	10.1	1.34
14	21	12	11	1.1	0.68	0.78	0.13	1.1	0.38	1.08	0.1	7.3	1.15
15	31	13	12	1.14	0.81	0.69	0.10	1.3	0.39	1.32	0.2	8.7	1.01
16	44	12	12	3.37	0.84	0.6	0.10	2.6	0.43	1.46	0.2	24.9	1.86
17	25	8	9	1.58	0.39	0.19	0.06	1.4	0.34	1.1	0.1	11.5	1.08
18	28	9	7	2.07	0.84	1.07	0.14	1.8	0.45	0.8	0.2	14.4	1.17
19	31	9	7	2.08	0.95	0.79	0.10	1.9	0.45	1.05	0.3	13.3	1.17
20	22	10	9	1.32	0.96	0.52	0.06	1.3	0.36	1.02	0.1	10.4	0.95
21	27	11	14	1.33	1.19	1.06	0.19	1.5	0.97	1.26	0.2	7.9	1.2
22	23	7	5	1.28	0.63	0.75	0.08	0.8	0.42	0.83	<0.1	16.9	1.33
23	24	8	7	1.61	1.04	0.07	0.05	1.0	0.49	1.08	0.1	15.1	0.84
24	29	9	9	2.24	0.53	2.36	0.19	1.9	0.38	0.91	0.1	13.2	1.64

Table 4. Concentration of lanthanide in pond sediment, mg/kg.

S. No.	Sc	Y	La	Ce	Pr	Nd	Eu	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
1	18.0	21.0	40.0	66.0	8.7	32.0	1.3	5.9	5.2	0.8	4.1	0.8	2.1	0.3	1.6	0.2
2	25.0	21.0	32.0	73.0	7.3	27.0	1.3	5.3	4.7	0.7	4.1	0.8	2.2	0.3	1.8	0.3
3	8.0	23.0	56.0	99.0	12.9	47.0	1.6	8.6	7.0	0.9	4.9	0.9	2.2	0.3	1.5	0.2
4	18.0	13.0	21.0	49.0	4.8	18.0	0.8	3.4	3.1	0.4	2.6	0.5	1.4	0.2	1.2	0.2
5	12.0	22.0	37.0	93.0	8.3	30.0	1.1	5.8	5.0	0.8	4.4	0.8	2.2	0.3	1.8	0.3
6	16.0	13.0	16.0	43.0	4.1	16.0	0.8	3.3	2.9	0.5	2.6	0.5	1.4	0.2	1.2	0.2
7	14.0	18.0	33.0	77.0	7.5	27.0	1.1	5.2	4.5	0.7	3.6	0.7	1.8	0.2	1.4	0.2
8	10.0	22.0	47.0	94.0	10.8	40.0	1.5	7.2	6.1	0.9	4.5	0.8	2.0	0.3	1.4	0.2
9	7.0	15.0	29.0	74.0	6.3	22.0	0.8	4.2	3.7	0.6	3.1	0.6	1.6	0.2	1.3	0.2
10	11.0	23.0	50.0	157.0	10.5	37.0	1.2	7.0	6.1	0.9	4.7	0.9	2.4	0.3	1.8	0.3
11	8.0	11.0	22.0	64.0	4.6	17.0	0.7	3.2	2.7	0.4	2.2	0.4	1.1	0.2	0.9	0.1
12	23.0	13.0	31.0	41.0	6.4	22.0	0.8	3.9	3.2	0.5	2.6	0.5	1.3	0.2	1.1	0.2
13	11.0	18.0	28.0	84.0	7.1	26.0	1.0	5.2	4.4	0.7	3.7	0.7	1.8	0.3	1.5	0.2
14	15.0	16.0	23.0	55.0	5.7	22.0	1.0	4.2	3.9	0.6	3.4	0.6	1.7	0.2	1.3	0.2
15	18.0	20.0	28.0	53.0	6.9	26.0	1.2	5.1	4.7	0.7	3.9	0.8	2.0	0.3	1.5	0.2
16	9.0	61.0	119.0	163.0	28.3	99.0	2.7	18.0	16.0	2.3	13.0	2.4	6.1	0.8	4.8	0.7
17	7.0	21.0	40.0	91.0	9.0	33.0	1.1	6.3	5.5	0.8	4.3	0.8	2.1	0.3	1.7	0.2
18	5.0	28.0	65.0	126.0	14.2	51.0	1.4	9.2	7.9	1.1	6.0	1.1	2.8	0.4	2.2	0.3
19	6.0	24.0	54.0	111.0	11.9	43.0	1.3	7.9	6.6	0.9	5.0	0.9	2.4	0.3	1.9	0.3
20	9.0	18.0	45.0	108.0	9.8	36.0	1.3	6.4	5.4	0.7	3.8	0.7	1.7	0.2	1.2	0.2
21	12.0	18.0	32.0	73.0	7.5	28.0	1.2	5.5	4.9	0.7	3.7	0.7	1.8	0.2	1.4	0.2
22	3.0	15.0	59.0	110.0	11.7	41.0	0.9	6.9	5.4	0.7	3.3	0.6	1.5	0.2	1.1	0.2
23	5.0	14.0	53.0	99.0	10.8	38.0	1.0	6.7	5.2	0.6	3.1	0.5	1.4	0.2	1.1	0.2
24	5.0	20.0	56.0	131.0	11.1	39.0	1.1	6.9	5.8	0.8	4.2	0.8	1.9	0.3	1.5	0.2

and Lu) was ranged from 82 - 431 and 8 - 46 mg/kg with mean value of 182 ± 30 and 15 ± 3 mg/kg, respectively. The ratio of LREE/HREE and Lu/Y was found to be in the range of 9 - 18 and 14 - 56 with mean value of 12 ± 1 and 27 ± 4, respectively. The concentration of REE and LREE/HREE and Lu/Y ratio were found to be higher than values reported in river sediments of the other regions of the World [3]-[11].

The concentration of Th and U in the sediments (n = 24) was ranged from 6.1 - 25 and 0.46 - 1.86 mg/kg with mean value of 11 ± 2 and 1.14 ± 0.13 mg/kg, respectively. The Th/U ratio was ranged from 6 - 28 with mean value of 11 ± 2. The concentration of actinide elements in the studied area was found to be comparable to values reported in soil of other regions of the country [12] [13] (**Figure 2**).

3.4. Spatial Variations and Sources

The sediment samples were collected from 24 ponds which situated in 11 locations (*i.e.* villages) of Ambagarh Chowki block. The content of the REE in the pond sediments of 11 locations are shown in **Figure 3**. The highest content of the REE in the pond sediment of Bhadsena was observed. The REE content in sediment was found to increase as the depth profile was increased from 0 - 30 cm, may be due to geogenic origin and less binding with organic components of the sediment, **Figure 4**.

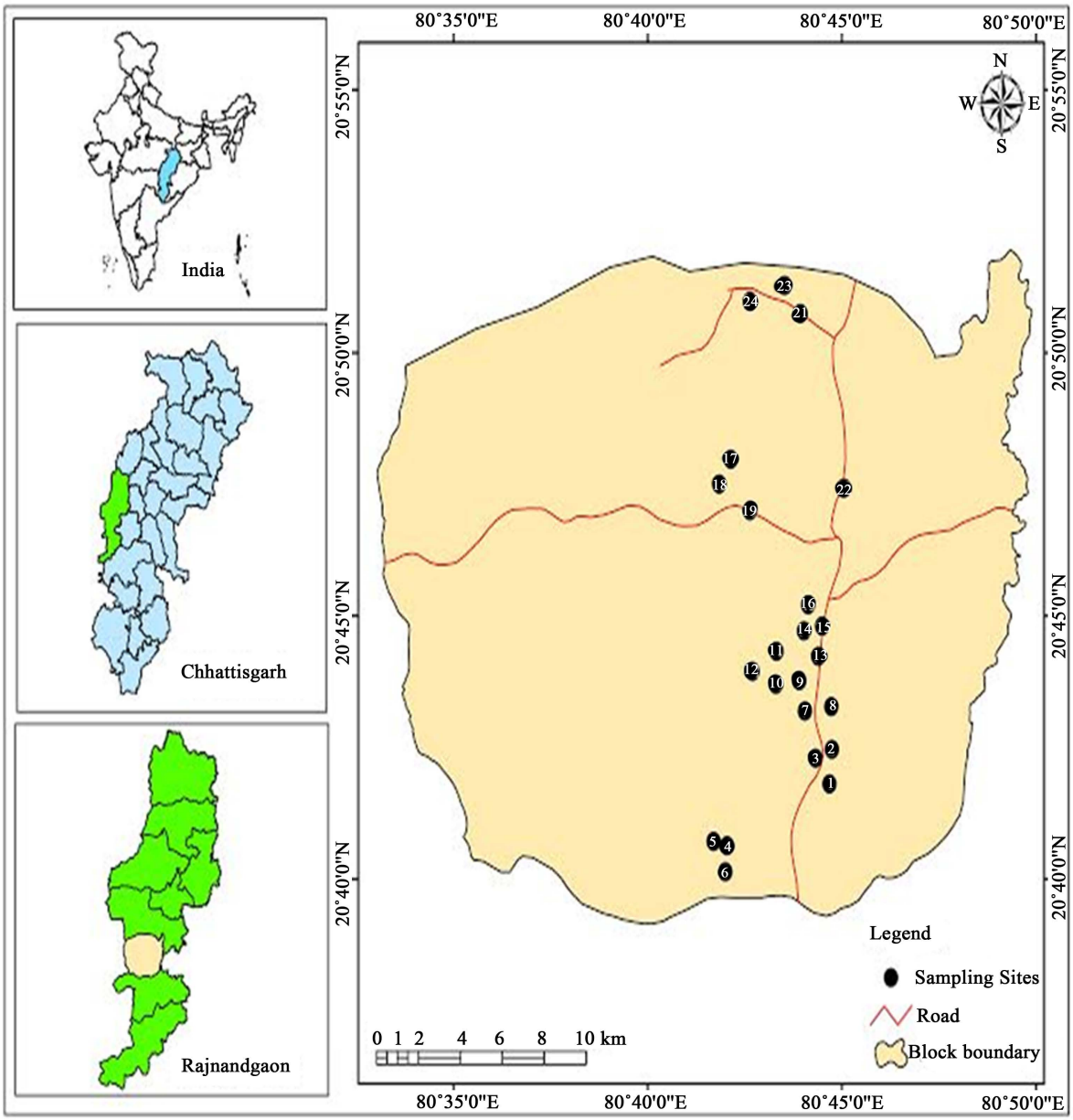
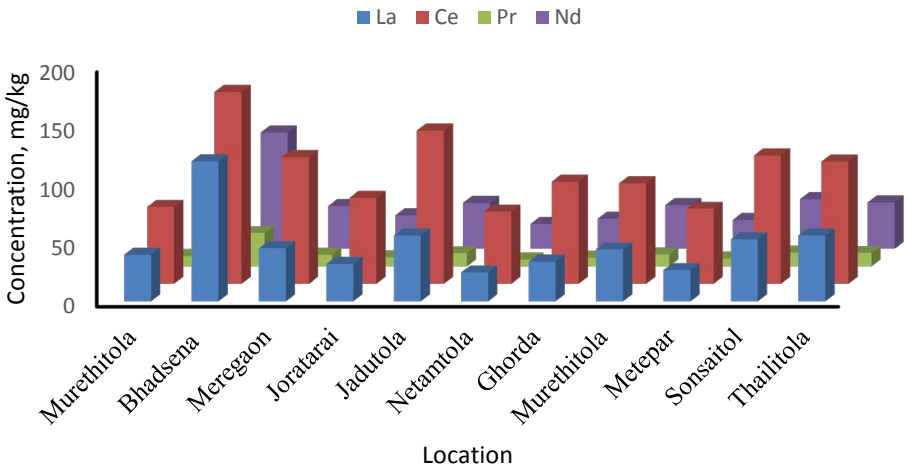


Figure 1. Representation of sampling locations (*i.e.* Murethitola-1, Murethitola-2, Murethitola- 3, Netamtola- 1, Netamtola-2, Netamtola-3, Kaudikasa-1, Kaudikasa-2, Kaudikasa-3, Ghorda-1, Ghorda-2, Ghorda-3, Metepar-1, Metepar-2, Metepar-3, Bhadsena, Sonsaitola-1, Sonsaitola-2, Sonsaitola-3, Meregaon, Joratarai,Thailitola-1,Thailitola-2 and Jadutola) in Ambagarh Chowki.

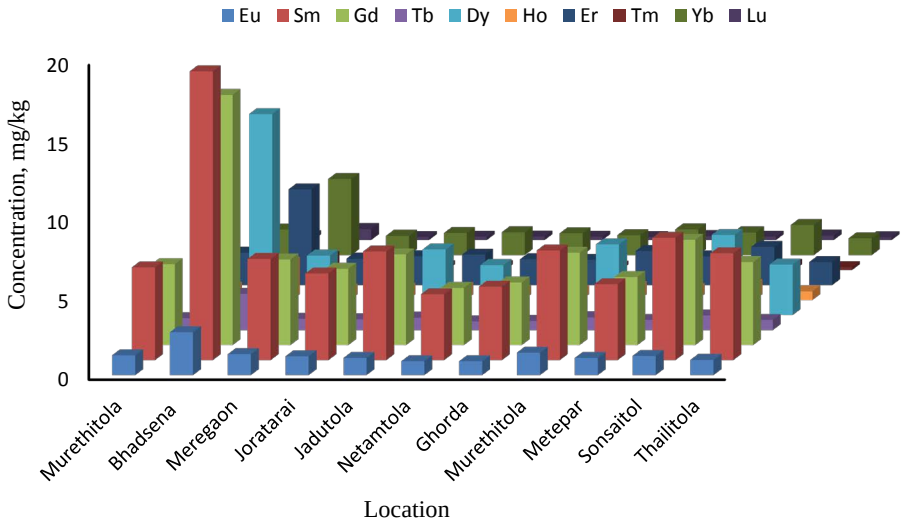
The correlation matrix of the REE is summarized in **Table 5**. All REE inclusive of Eu, Th and U are correlated well in the sediment, indicating origin from the similar sources likely to geogenic origin. They were partially correlated with elements *i.e.* Be, K, Rb, Cs, Mo, As, Sb, Bi, Sn, and Ag. Their negative correlations with elements *i.e.* Na, Mg, Ca, Ba, Sr, Al, Ga, V, Cr, Fe, Mn, Co, Ni, Cu, Zn, Cd and Pb were observed.

3.5. Enrichment

The E_f value for Sc, Y, La, Ce, Pr, Eu, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and U in the sediment was ranged from 0.8 - 4.2, 1.5 - 9.4,1.7 - 13, 1.4 - 12, 1.7 - 13, 1.6 - 9,1.7 - 12, 1.6 - 12, 1.9 - 13, 1.6 - 11,1.6 - 11, 1.6 - 9, 1.4 - 9, 1.4 - 9, 1.4 - 8, 1.1 - 7, 1.1 - 11 and 0.4 - 3 with mean value of 2.5 ± 0.4, 4 ± 1, 6 ± 1, 5 ± 1, 5 ± 1, 4

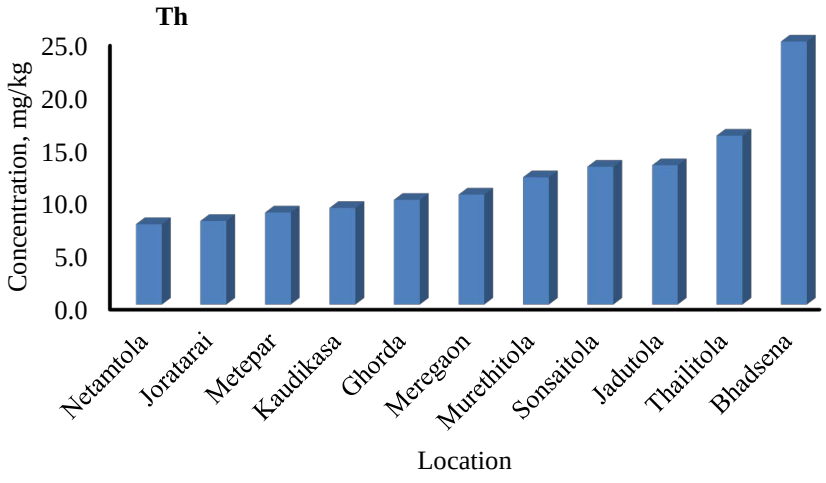


(a)

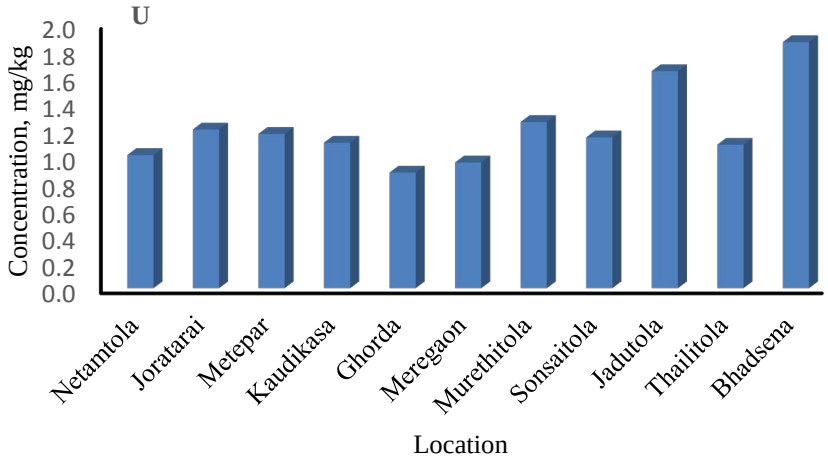


(b)

Figure 2. Spatial variation of REE concentration in sediment of Ambagarh Chowki.

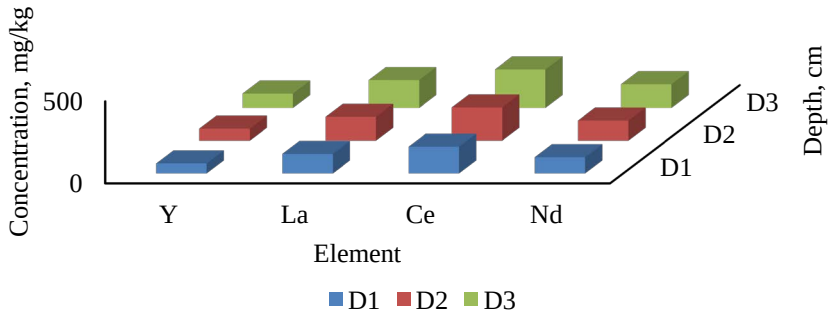


(a)

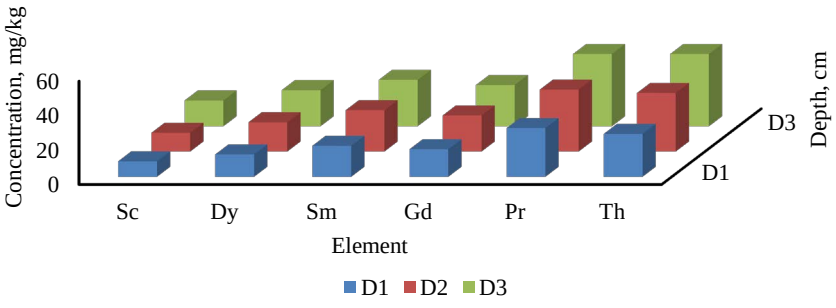


(b)

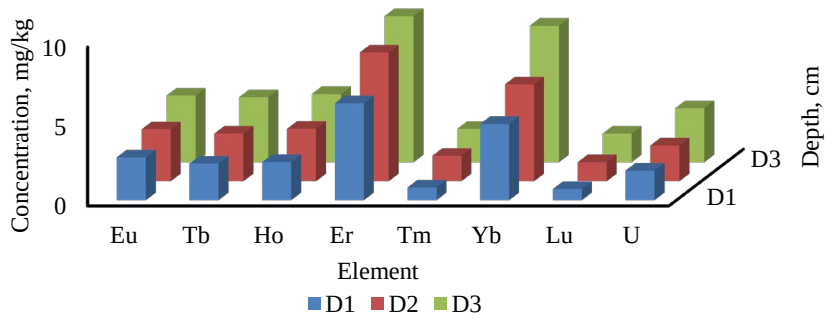
Figure 3. Spatial variation in concentration of actinide in sediment.



(a)



(b)



(c)

Figure 4. Depth profile studies of elements in Bhadsena pond sediment. D1 = 0 - 10 cm, D2 = 10 - 20 cm, D3 = 20 - 30 cm.

Table 5. Correlation matrix of REE.

	La	Ce	Pr	Nd	Eu	Sm	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
La	1.00													
Ce	0.84	1.00												
Pr	0.99	0.80	1.00											
Nd	0.99	0.80	1.00	1.00										
Eu	0.84	0.63	0.90	0.91	1.00									
Sm	0.97	0.78	0.99	1.00	0.93	1.00								
Gd	0.95	0.76	0.98	0.99	0.94	1.00	1.00							
Tb	0.92	0.72	0.96	0.96	0.95	0.98	0.99	1.00						
Dy	0.89	0.69	0.94	0.94	0.94	0.96	0.98	1.00	1.00					
Ho	0.87	0.67	0.92	0.93	0.94	0.95	0.97	0.99	1.00	1.00				
Er	0.85	0.65	0.91	0.91	0.93	0.94	0.96	0.99	1.00	1.00	1.00			
Tm	0.83	0.64	0.89	0.89	0.90	0.92	0.94	0.98	0.99	0.99	1.00	1.00		
Yb	0.81	0.61	0.87	0.87	0.89	0.91	0.93	0.97	0.98	0.99	0.99	1.00	1.00	
Lu	0.83	0.63	0.89	0.89	0.90	0.92	0.94	0.97	0.98	0.99	1.00	1.00	1.00	1.00

± 1, 5 ± 1, 5 ± 1, 5 ± 1, 4 ± 1, 4 ± 1, 4 ± 1, 3 ± 1, 3 ± 1, 3 ± 1, 3 ± 1, 4 ± 1 and 1.7 ± 0.3, respectively. They were moderately enriched in the sediment. Their highest enrichments were marked in sediment of the Bhadsena village.

4. Conclusion

The REE were moderately enriched in all ponds and their enrichments were found to decrease as the mass number of the REE was increased. The concentration of all REE in the sediment was increased vertically, may be due to origin from the rock weathering. Their highest contents were marked in the sediment of Bhadsena village, Rajnandgaon, India.

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