Rare Earth Elements in Soils of Jharia Coal Field

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Abstract—There are many sources trough which the soil get enriched and contaminated with REEs. The determination of REEs in environmental samples has been limited because of the lack of sensitive analytical techniques. Soil samples were collected from four sites including open cast coal mine, natural coal burning, coal washery and control in the coal field located in Dhanbad, India. Total concentrations of rare earth elements (REEs) were determined using the inductively coupled plasma atomic absorption spectrometry in order to assess enrichment status in the coal field. Results showed that the mean concentrations of La, Pr, Eu, Tb, Ho, and Tm in open cast mine and natural coal burning sites were elevated compared to the reference concentrations, while Ce, Nd, Sm, and Gd were elevated in coal washery site. When compared to reference soil, heavy REEs (HREEs) were enriched in open cast mines and natural coal burning affected soils, however, the HREEs were depleted in the coal washery sites. But, the Chondrite-normalization diagram showed significant enrichment for light REEs (LREEs) in all the soils. High concentration of Pr, Eu, Tb, Ho, Tm, and Lu in coal mining and coal burning sites may pose human health risks. Factor analysis showed that distribution and relative abundance of REEs of the coal washery site is comparable with the control. Eventually washing or cleaning of coal could significantly decrease the emission of REEs from coal into the environment.

Keywords—Rare earth elements, coal, soil, factor analysis

I. INTRODUCTION

IN geochemistry, the 17 rare earth elements (REEs) include scandium (Sc), yttrium (Y), and the lanthanides. Lanthanides are lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) REEs can be divided into two sub-groups: light and heavy REEs. The distinction is based on their charge and ion radius which in turn guide their physico-chemical behavior. The light REEs (LREEs) are La, Ce, Pr, Nd, Pm, Sm, and Eu, and all other elements belong to the group of heavy REEs (HREEs) [1]. REE concentrations in surface soils vary according to parent material properties, history and weathering state of the soil, contents of organic matter (OM) and clay minerals, etc. There are many sources through which the soil gets enriched and/or contaminated with REEs. The production and use of phosphate fertilisers may cause REEs release both to the atmosphere and to the soil [2].

Petroleum-cracking catalysts and their products in oil-fired power plants and oil refineries are other sources of REE pollution. The cracking products are produced from REE-rich minerals (bastnaesite and monazite, Tyler 2004).

Rare earth elements in coal appear to consist of a primary fraction which is associated with syngenetic mineral matter [3, 4]. Another portion of the REE can be externally derived or mobilized when primary mineral matter is disintegrated or altered during coalification process and may be retained in the coal bed but redistributed and incorporated into other mineral components (authigenic minerals). REEs are enriched in coals in the Huaibei Coalfield (China) as compared with U.S. coals and the world coal average [5]. Due to different coal-forming paleoenvironments and geologic settings, some coals are enriched in HREEs relative to LREEs, whereas some are enriched in LREEs [6]. Many coals worldwide are slightly enriched in HREE relative to LREE as compared with chondrites and shales. A factor contributing to this fractionation could be the ability of the HREE to form complexes with organic compounds which are more stable than those of the LREE. The various processes of coal extraction and conversion/utilization like mining, coal burning (natural or anthropogenic), coal washing etc. may also affect the distribution, bioavailability and ultimate fate of REEs.

There has been global attention to the effects of REEs on human health; however, there are only few studies in this regard. [7] derived thresholds for REEs in water from general literature and inferred that two of the three locations exceeded the threshold for a number of REEs and possible health risks for humans could not be ruled out. [8] found that the children born and growing up in LREEs mining area had a noticeable enrichment of REEs with a majority of LREEs such as La, Nd, and Pr in their scalp hair. Some children had a considerably high degree of enrichment which was considered as a high-risk group with LREEs (mainly La and Nd) exposure. Toxic effects of REEs and several adverse effects due to occupational and environmental exposure to REEs have been reported [9, 10, 11]. The substitution of REE especially Eu for calcium occurs in both geological and biological environments due to the size similarity of their atomic radii (for Eu, it's mainly the oxidation state). In human bodies, the significant role of Ca in cellular activity may be affected by the presence of REE and the subsequent modification of cellular interactions [12]. The toxicity of REE decreases as atomic number increases, apparently due to greater stability of the heavy rare earth elements (HREE) [13]. There are only few studies on the effects of REEs exposure on humans.The determination of REEs in environmental samples has been

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limited because of the lack of sensitive analytical techniques. Only very few data are available on the status of REEs particularly in Indian soils. Till date no study has been carried out in the soils affected by coal based industries. Thus this study is aimed to determine the content and enrichment of REEs in the soils of Jharia coalfield.

II. MATERIALS AND METHODS

The study sites are active coal mines and other coal industries located in Jharia coalfield of Dhanbad, India (Fig. 1). The coalfield lies in the Damodar River Valley, and covers about 110 square miles (280 square km), and produces bituminous coal suitable for coke making. Most of India's coal comes from this region. Geologically the area is comprised with Archean granites and gneisses. Entisols, Inceptisols and Alfisols are the predominant soil types in this region. The sampling sites includes: (i) Opencast coal mine- The Bhowra site is an active surface coal mine area in which there are many small open cast coal mines. Bhowra is located at 23°40'N 86°24'E, with an average elevation of 153 m; (ii) Natural coal burning site: Lodna fire affected area is under the Jharia coalfield fire that has been burning underground for nearly a century. The first fire was detected in 1916. It is located at 23°43'N 86°26'E with an average elevation of 180 m; (iii) Coal washery: The two coal washeries are located at Pathardih and Sudamudih. Pathardih is located at 23°40'N 86°25'E with an average elevation of 171 m. Sudamudih is located at 23°39'N 86°25'E with an average elevation of 149 m; and (iv) Control site: Chandankiari is about 10 Km away from the above coalfields, located at 23°34'N 86°21'E with an average elevation of 174 metres. The soils in the control site are mostly barren lands. Soil samples (0-15 cm) were collected during November 2008.
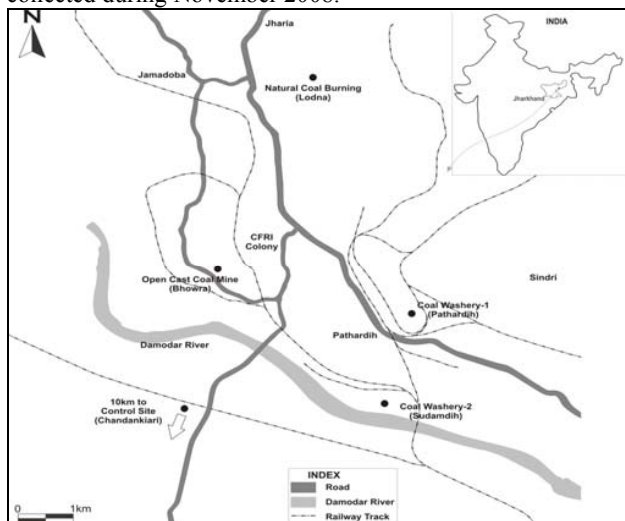

Fig. 1 Location of sampling sites in the Jharia coalfield (Dhanbad, India).

For determination of REEs, soil samples (0.05 g) were digested in a PTFE Teflon beakers using acid mixture (containing 7:3:1 $HF-HNO_3-HClO_4$) at ~ 200 °C for about 1 hour. One ml of 5 $\mu g\ ml^{-1}$ Rh solution was added to act as an internal standard. The REEs content in the digested solution were measured using an ICP-MS (make Perkin Elmer). The detection limit was up to 0.004 ng g^{-1}.The data were analysed for correlation and factor analysis using the statistical software SYSTAT-12.

III. Results and discussion

A. REEs Concentration of Soil Samples

Concentrations of REEs in the coalfield of Jharia are summarized in Table 1. As shown in Table 1, the average concentrations of La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Tm, Lu, Ho and Sc in open cast mine sites were higher as compared to the control soils. The average concentrations of Sm, Nd Sc, Ce and Gd in the coal burning; Sm, Ce, Nd, Gd, Er and Sc in the coal washery sites were slightly elevated as compared to the reference values. However, there are many differences in the total concentrations of REEs in soils studied. The average total content of REEs (∑REE) in opencast coal mine soil is the highest (222.0 mg/kg), followed by control (203.1), coal washery-1 (192.3) coal burning (169.4), and coal washery-2 (162.5). Y has significantly contributed for the higher ∑REE observed under control; the level of Y in other soils is depleted up to 60%. These soils are developed from granite/ gnesis parent material. [14] found that soil developed from the granite parent material has the highest REEs followed by basalt and red siltstone. The concentrations and distribution of REEs in soil depends on its content in the original parent rocks, mineralogical assemblages of the weathering crusts, pH value, oxidization reduction conditions, rain, underground water and organisms in the profiles [14]. Total REEs was the highest in the opencast mine soil, which is probably due to the higher amount of coal deposition in these soils as compared with coal washery and burning sites. Coal is basically organic materials which could retain the REEs through various reactions. Organic matter has many negatively charged groups per unit dry weight, and a high capacity to adsorb or chelate divalent and trivalent cations. REE concentrations of A horizon (surface soils) are higher than that of the sub soils, which is probably due to the biological effect in topsoil [15, 16]. In the coal burning sites, formation of iron oxides during coal burning may also retain the REEs.

The ∑LREE/∑HREE ratio for the different types of soil varies from 1.8 to 3.2, which suggests that LREEs are more abundant in these soils. With the soil developing intensively, LREE gain and HREE deplete [17]. HREEs are more likely to have more mobility than LREEs. Thus LREEs are enriched and HREEs are depleted gradually during the migration process. In our study, this ratio was slightly higher in all the coal contaminated soils (2.4 – 3.2) as compared with the control (1.8). Many previous studies show that coal is slightly enriched in HREEs relative to LREEs [6]. The possibility of coal admixture to soil is more in the open cast coal mine soils due to the continuous dispersal of coal from mines and its ultimate deposition on soils. The LREEs enrichment is relatively lower in opencast mine soils (∑LREE/∑HREE –

2.4) than other soils (2.9 to 3.2) which is probably due to the HREEs contribution from the coal particles admixed with soil. [5] have reported variations in the abundance of REEs in the samples from different mines, between different coal seams, and within individual coal seams. Though pure coal is enriched in HREE, some coals have relatively higher LREEs

during the process of coal formation and weathering. Chondrite-normalized REE patterns show that the coal ash has shale-like LREE enrichment [12]. The behaviour and probable fractionation of the REE in the coal forming process may be strongly affected either side in the presence of other ions, e.g., bicarbonate anions, and especially by simultaneous

TABLE I

CONCENTRATION OF REES (MG/KG) IN THE SOILS OF JHARIA COAL FIELD, DHANBAD

No	Control			Open cast mine			Natural coal burning			Coal washery-1			Coal washery-2		
	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
La	40.05	11.23	103.99	59.40	24.41	153.06	31.53	22.12	50.49	39.78	23.44	75.90	29.09	13.81	51.20
Ce	53.02	6.04	157.67	49.34	9.38	104.83	57.81	36.87	99.39	66.53	7.97	125.18	55.68	26.29	99.06
Pr	10.93	2.55	41.68	19.16	5.06	59.52	6.63	4.54	10.97	8.59	4.52	28.83	6.23	2.85	11.24
Nd	20.83	4.82	57.64	22.06	6.58	42.75	25.05	17.22	41.50	25.84	5.54	53.48	23.79	10.39	42.65
Sm	4.30	0.98	11.07	4.41	0.94	8.47	5.02	3.29	7.80	4.90	0.97	8.86	4.96	2.06	9.08
Eu	1.77	0.55	7.12	2.95	0.75	9.22	0.93	0.69	1.54	1.15	0.60	4.45	0.81	0.40	1.10
Gd	3.45	0.66	9.03	3.39	0.73	6.99	3.84	2.50	6.17	3.92	0.68	6.48	3.83	1.67	6.87
Tb	1.45	0.29	6.08	2.36	0.49	8.06	0.62	0.39	0.99	0.81	0.40	3.62	0.64	0.29	1.13
Dy	3.31	0.95	6.59	3.26	0.83	6.11	3.54	2.03	5.59	3.38	0.87	4.50	3.74	1.67	6.26
Ho	1.22	0.49	2.79	1.53	0.70	3.53	0.86	0.47	1.38	0.89	0.55	1.50	0.92	0.42	1.46
Er	1.60	0.38	3.76	1.45	0.31	2.89	1.56	0.90	2.51	1.43	0.32	1.82	1.70	0.76	2.78
Tm	0.91	0.24	3.65	1.28	0.30	4.18	0.35	0.19	0.57	0.39	0.21	1.65	0.38	0.15	0.64
Yb	2.10	0.30	5.48	1.68	0.23	3.66	1.91	1.17	3.01	1.57	0.22	2.06	2.10	0.89	3.44
Lu	1.01	0.19	4.67	1.98	0.22	7.17	0.27	0.17	0.44	0.35	0.15	2.48	0.30	0.12	0.51
Sc	10.06	5.04	21.78	21.23	11.25	81.59	11.27	9.27	15.69	12.73	9.14	15.65	8.79	6.20	10.79
Y	47.09	10.84	176.52	26.58	15.09	46.47	18.15	10.39	28.51	20.06	13.59	23.95	19.50	8.76	31.31
ΣREE	203.1			222.0			169.4			192.3			162.5		
ΣLREE	130.9			157.3 (1.2)			127.0 (1.0)			146.8 (1.1)			120.6 (0.9)		
ΣHREE	72.2			64.7 (0.9)			42.4 (0.6)			45.5 (0.6)			41.9 (0.6)		
ΣLREE/ΣHREE	1.8			2.4			3.0			3.2			2.9		

*Figures in parenthesis are their respective normalization with control

with control flocculation of the organic colloids with hydrous iron oxides [18]. Thus in our study, the high background LREEs in the original soils and the weathering and redistribution of the coal particles in the soil matrix might have resulted in differential relative enrichment patterns of LREE.

A chondrite-normalization method is often applied to study the distribution patterns of REEs using the concentration provided by [19]. The chondrite-normalized REEs pattern is given as the logarithm of the normalized abundance versus atomic number. The chondrite-normalized REEs patterns of different soils are shown in Fig-2. The chondrite normalized REEs distribution pattern curves downward from left to right. The REEs patterns are characterized by LREE-enrichment and HREE-depletion. The increase in REEs in the soil is consistent with the observations of [20]. The REE patterns of soil from the surface and sub soil of the steeply eroded soils are similar and display progressive LREE enrichment [21]. The factors responsible for the retention of LREEs in soils are possibly due to preferential sorption onto Fe oxides [22, 23] as well as clay minerals [24]. REEs of coal burning and washery soils are characterised by three parallel distribution pattern

curves. But this phenomenon is not observed in the opencast mine soils, where, all the LREEs and some HREEs (Tb, Ho, Tm, and Lu) are enriched. Several investigations on REE distribution patterns in coal reveal slight enrichment of HREE relative to LREE as compared with chondrites and shales [18]. Chondrite-normalized patterns for a suite of about 300 samples from Bulgarian coal deposits showed relative enrichment of HREE against LREE as compared with sedimentary rocks [18]. Though coal is enriched with HREEs, specific accumulation of HREEs in washery and burning sites could not be observed. In washery sites there is possibility of soil contamination with washery rejects comprising relatively higher amount of mineral matter after beneficiation of coal. Obviously, the mineral rich washery rejects are deficient in HREEs. Also under coal burning sites the burnt residues are left over, not the organic matrix of coal. However, in the opencast mine soils coal particles as such are admixed with soils which are considered to have relatively more organic matter than washery rejects. Thus, the REE pattern in the soils surrounding the coal industries supports the nature of soil contamination.
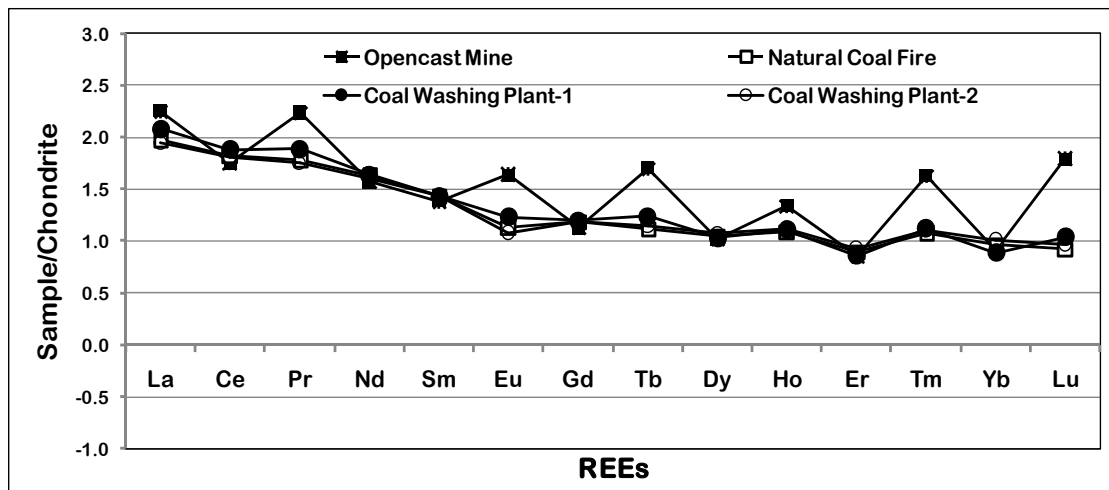
Fig. 2 Chondrite normalized diagram showing the distribution patterns of REEs of the soil in the Jharia coalfields.

The anomaly of Eu is defined by the ratio of $\delta Eu = Eun/Eun*(Eun* = (Smn + Gdn)/2)$. Negative anomalies of Eu were observed for soils of coal burning (0.86), and coal washery- I & II (0.93 & 0.82) sites. Positive Eu anomaly was observed for open cast mine soil (1.3). Positive Eu anomaly in mine soils shows the preferential addition of Eu to soils from the coal particles deposited. The chondrite normalized REEs distribution patterns for the profiles derived from latosol show slightly negative Eu anomaly with δEu ranging from 0.72 to 1. The Eu negative anomalies was more obviously observed in the soils profiles developed from limestone, granite, eolian red sand, and mica schist, showing V-type distribution patterns (Miao et al. 2007). Eu occurs partly as Eu^{2+} which differs from the trivalent REEs, so its concentration is mostly controlled by the parent properties, contents of organic matter and clay mineral in the tropical laterites during the stages of weathering [25].

B. Factor Analysis

It was possible with factor analysis to get associations of REEs in factors that would give some information about the source and the behaviour of contamination. This technique attempts to reveal the correlation structure of the variables allowing interpretation of geological processes affecting the geochemical data. Factor analysis was performed by evaluation of principal components and computing the eigenvectors. Two factors described the satisfactory occurrence of REEs in these soils (Fig 3). These factors explained to a relatively large extent the total variance (85.08%) of the variables used in the analysis. Ho, Sm, Tb, Lu, and Y showed a strong association with the first factor (F1) (62.11%), and correlation analysis also showed significant correlations between them (P < 0.001; Table 2), which indicated that these above REEs might have originated from the common source. Pr, Tm, Eu, and Er showed a strong association with the second factor (F2) (40.63%), and correlation analysis also showed significant correlations between most of these REEs (P < 0.001; Table 2).
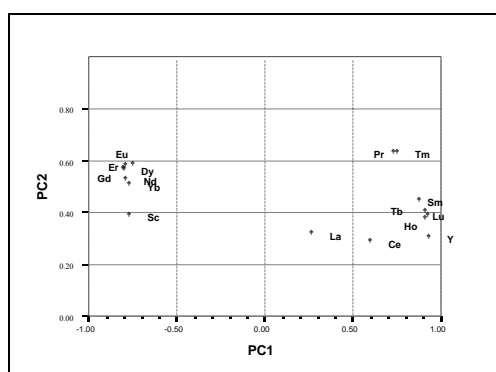

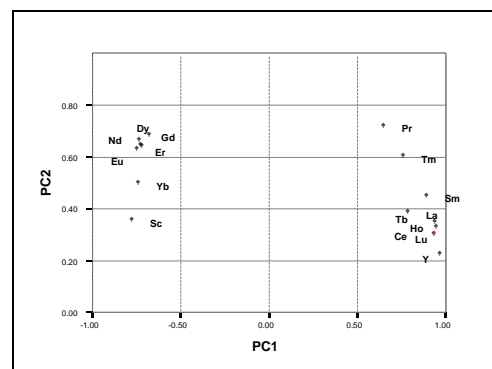Fig. 3 Component loadings calculated for REEs

Fig 4 Principal component plots of individual sites. (a) Control

TABLE II
CORRELATION COEFFICIENT MATRIX BETWEEN REES (N = 90)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y
La	1.00															
Ce	0.13	1.00														
Pr	0.33**	0.50**	1.00													
Nd	-07	-0.34**	-0.19	1.00												
Sm	0.34**	0.54**	0.96**	-0.44**	1.00											
Eu	-0.04	-0.31**	-0.12	0.97**	-0.37**	1.00										
Gd	-0.05	-0.33**	-0.19	0.97**	-0.43**	.99**	1.00									
Tb	0.33**	0.59**	0.93**	-0.51**	0.99**	-0.44**	-0.50**	1.00								
Dy	-0.07	-0.33**	-0.20	0.97**	-0.45**	0.98**	0.99**	-0.51**	1.00							
Ho	0.32**	0.64**	0.91**	-0.53**	0.98**	-0.47**	-0.52**	0.99**	-0.53**	1.00						
Er	-0.04	-0.29**	-0.25*	0.88**	-0.46**	0.87**	0.92**	-0.50**	0.94**	-0.50**	1.00					
Tm	0.33**	0.64**	0.89**	-0.31**	0.91**	-0.25*	-0.28**	0.92**	-0.28*	0.94**	-0.20	1.00				
Yb	-0.06	-0.27*	-0.32**	0.78**	-0.49**	0.76**	0.83**	-0.51**	0.86**	-0.52**	0.97**	-0.20	1.00			
Lu	0.30**	0.68**	0.85**	-0.55**	0.94**	-0.49**	-0.53**	0.96**	-0.54**	0.99**	-0.49**	0.95**	-0.48**	1.00		
Sc	-0.10	-0.29**	-0.41**	0.68**	-0.55**	0.66**	0.74**	-0.56**	0.77**	-0.56**	0.90**	-0.25	0.98**	-0.51**	1.000	
Y	0.29**	0.57**	0.86**	-0.59**	0.95**	-0.53**	-0.58**	0.96**	-0.58**	0.97**	-0.55**	0.89**	-0.55**	0.96**	-0.575**	1.000

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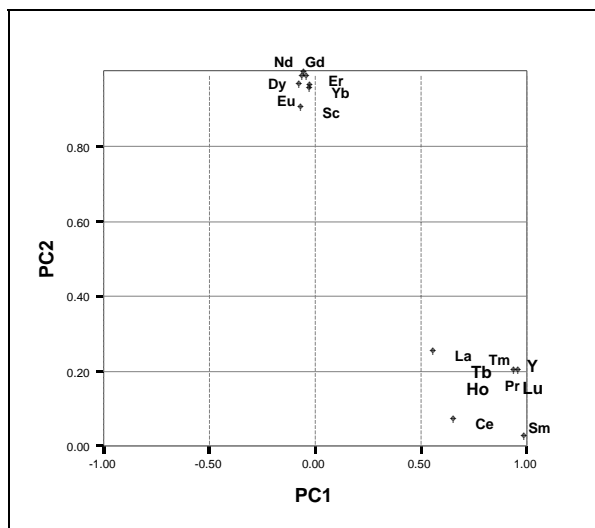

Fig 4 Principal component plots of individual sites (b) Coalfield soils (opencast coal mine, coal washery and natural coal burning sites)

Factor analysis was done separately for the control and contaminated soils and the results are plotted in Fig-3. Distinct differences could be observed from the PCA plots. The pattern was slightly scattered in control, whereas it tends to form two groups in the contaminated soils (Fig-4). ND, Eu, Gd, Dy, Er, Yb, and Sc are clustered together in the coal contaminated soils, whereas Yb and Sc from the above group are delinked in the control soils. In the second group (La, Tm, Ce, Pr, Sm, Ho, Lu, Tb, and Y), Pr and Tm are delinked in case of control soil. From the above discussion it is inferred that the distribution and association REEs are disturbed in the soils of Jharia coalfield when compared with the control soil. REEs enrichment in the opencast coal mine soils are in the order Sc > Lu > Pr > Eu > Tb > La > Tm > Ho > Nd. In the coal burning (Sm, Nd, Sc, Ce, and Gd) and washery (Sc, Ce, Sm, Nd, Gd, Dy, and Er) soils a slight enrichment in some of the REEs was observed. Depletion of Y (up to 60%) in all the coal affected soils and specific depletion of Tb, Tm and Lu in washery and burning sites were noticed.

III. CONCLUSION

Coal mining activities caused enrichment of REEs in the nearby soils. There are significant differences in chondrite-normalized REE patterns between the soils of Jharia coalfield. Open cast coal mine soils are enriched with La, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Tm, Lu, Ho and Sc, soils of coal washery and coal burning sites are enriched with Ce, Nd, Sm, Gd, Dy and Sc. The total content of REEs ($\sum$REE) was highest in the opencast coal mine soils followed by soils under control, coal washery-1, coal burning and coal washery-2 sites. Negative Eu anomaly was found for coal burning and washery sites, however, positive Eu anomaly for mine soils. Factor analysis showed that REEs distribution pattern in the soils affected by coal based industries is significantly different than the control soils. Further studies are to be performed to determine the bioavailability and mobility of these REEs in the soils of Jharia coalfield, to understand the bioaccumulation of REEs in plants from soils, and human exposure risks.

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