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Variation of REE content in the soil affected with the Paper Mill waste at Manikpara, Jhargram, India.

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ABSTRACT:

Coal fly ash has been regarded as the possible source of REE (rare earth element) toxicity in the soil. Untreated discharge of Pulp-and-paper mill wastes containing REE of the coal fly ash and their concentration augmentation in the soil through adsorption into the secondary mineral and/or chelation with the effluent is a severe concern due to its impact into the surrounding environment. This study mainly examines the variation of REE content in the soil due to the accumulation of waste surrounding the paper mill located at Manikpara, Dist. Jhargram, W.B., India. Upper layer (0-15 cm depth) soil samples are collected from the four sites (Site-1,2,3,4) of different distance from the paper mill. Total soil REE concentrations are determined using ICPMS to study the enrichment status in the soil. The average total content of REEs in ppm (i.e. \sum REE) and pH of Site-4 (187.55, pH 8.14), Site-3 (176.523, pH 8.04), Site-2 (147.676, pH 6.7) and the control site (Site-1) (107.345, pH 6.27) indicate that soil REE content decreases with distance from the paper mill and increases with the pH of the soil. Chondrite-normalisation diagram confirms that significant enrichment for light REEs (LREEs) compare to the heavy REEs (HREEs) arises of all the studied soil. High Europium anomaly indicates adsorption of Eu on the Kaolinite clay mineral readily available in these soil originated by the chemical weathering of the original rock feldspar. The REE patterns of the upper layer soil in the vicinity of the paper mill confirm that the paper mill is a major source of REE contamination in the surrounding environment.

KEYWORD: Rare earth elements, Coal fly ash, Chemical weathering.

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INTRODUCTION:

The rare earth elements (REE) are identified by the International Union of Pure and Applied Chemistry (IUPAC) as a group of 17 elements having similar physicochemical characteristics including 14 Lanthanoids (Z=57-71) and Scandium (Sc, Z=21) and Yttrium (Y, Z=39) ¹. The elements comprising the Lanthanide series: Lanthanum (La, Z=57), Cerium (Ce, Z= 58), Praseodymium (Pr, Z= 59), Neodymium (Nd, Z= 60), Promethium (Pm, Z= 61), Samarium (Sm, Z= 62), Europium (Eu, Z= 63), Gadolinium (Gd, Z= 64), Terbium (Tb, Z= 65), Dysprosium (Dy, Z= 66), Holmium (Ho, Z= 67), Erbium (Er, Z= 68), Thulium (Tm, Z= 69), Ytterbium (Yb, Z= 70), and Lutetium (Lu, Z= 71). REEs are classified into two groups: the light earth elements (LREE: La, Ce, Pr, Nd, Pm, Sm, Eu) and all other REEs belong to the group of heavy rare earth elements (HREE) ². Promethium is virtually non-existent due to rapid radioactive decay (half-life is 2.62 years) ³.

The variations of total REE contents in the surface soils are highly dependent on the types of soil and of parent material from which they are issued ⁴⁻⁶. Other REE sources in which the soils got enriched and/or contaminated are atmospheric depositions (atmospheric particles, rainwater, and snow) and anthropogenic spreading (waste samples, irrigation, and sewage waters, and especially P containing fertilizers) ⁷. With the growing pulp and paper mill every year the amount of waste is being generated proportionately. Untreated waste like coal fly ashes, green liquor dregs, slaker grits, lime mud and pulp mill sludge of wastewater treatment plants contain various organic and inorganic substances ⁸. Improperly disposed of this waste have a significant environmental impact by damaging nearby water, soil, and air. Coal fly ash as a waste generated from the combustion of coal readily used in the Papermill has been regarded as a promising source for REE ⁹. Coal fly ash enriched with several times higher REE contents than that found in the raw coal ¹⁰. Many REE compounds show catalytic, magnetic, optical properties which expanded their application in different fields like in the production of LCD and plasma screens, fiber optics, lasers ¹¹ fertilizers ¹². The growing use of REEs leads to environmental contamination and therefore considered as emerging pollutants ^{13, 14}. Several reports have published about the toxic effects of REE in bacteria ¹⁵, plants ¹⁶ and animals ¹⁷⁻¹⁹. Numerous industrial sources enable REEs to penetrate into the human body also and therefore investigations of their effect on human health have been thriving globally. Bioaccumulation of REE among the residents at a different distance from the REE ore mining site indicates the associated environmental impact ²⁰. A significant role of Ca⁺² in different cellular activity in the human body has been affected by the REE⁺³ ions, due to the similarity of their radii. La⁺³, Dy⁺³ can affect the activity of enzymes like Ca⁺²-ATPase & Mg⁺²-ATPase, Eu³⁺ and Tb³⁺ inhibit calcineurin, La⁺³ and Gd⁺³ ions block different Ca channels in the human cell ²¹. So the determination of REE in environmental samples is important in order to find out the possible impact.

Till date, no studies have been carried out for REE enrichment in the soil affected with paper mill waste. Thus this study is aimed to determine the enrichment of REE content in the soil surrounding the paper mill located at Manikpara, India.

MATERIALS AND METHOD:

The paper mill is located in Manikpara, Dist. Jhargram, West Bengal, India at a distance of about 26 Km from IIT, Kharagpur. Geographically Manikpara is located at 22° 22' N latitude and 87° 7' E longitude with an average elevation of 73 meter. Soils of sites (-4,-3,-2) having been irrigated with effluent/solid waste from the paper mill for more than 5 years are selected for the study. Soil from the site-1 (control site) was obtained from a location remote from the paper mill and far removed from the influence of effluent/ solid waste. The distance of site-1, site-2, site-3 and site-4 from the paper mill are 3 Km, 1 Km, 750 meter, 500 meter, respectively. 4 soil samples (0-15 cm) from each site were collected during June-2018.

REE content were measured on a Thermo Fisher Scientific iCAP-Q quadrupole Inductively Coupled Plasma Mass Spectrometer (ICPMS) at the Radiogenic Isotope Facility of the Department of Geology and Geophysics Indian Institute of Technology (IIT) Kharagpur. The soil sample was powdered in a planetary mill and dried overnight at 100 °C in the oven (ca. 50 mg) were digested using a mixture of suprapure (3:1) 24 M hydrofluoric acid : 14M nitric acid on a hot plate at 120 °C for two days, then evaporated with two repetition. The samples were fluxed with a mixture of nitric acid and hydrogen peroxide for 12 hours (5 drops of H₂O₂ + 3ml HNO₃) on the hot plate at 120 °C. The samples were then dried and dissolve in 3 ml HNO₃. The final digested samples were diluted to 100 ml in 2% HNO₃ with 10 ppb Indium (In) as an internal standard and taken up in pre-cleaned 100 ml HDPE bottles. The procedural blanks were also prepared using the same protocol. The international rock standards (JG-2 and JB-3; granite and basalt) were also digested together with the samples. Prior to analyses, the samples were centrifuged and an aliquot from the supernatant used for analyses. The solutions were measured using the standard sample introduction system on the quadrupole ICPMS. The sample solutions were introduced to a Peltier-cooled glass cyclonic spray chamber with the help of peristaltic pump and PFA nebulizer with flow rate of 100µL/min. The mass spectrometer was optimized for maximum sensitivity using a custom 1 ppb multi-element solution on the masses ⁷Li, ⁵⁸Co ¹¹⁵In, ¹⁴²Nd, ²⁰⁸Pb, ²³²Th, and ²³⁸U covering the entire mass range. The oxide production was monitored on ¹⁴⁰Ce¹⁶O/¹⁴⁰Ce and ranges between 1.5 and 2%. The concentrations were calculated using the calibration curve method using the rock standards digested together with samples. For each element the calibration curve is forced through blank.

All statistical data were analysed using SPSS software version 16.

RESULTS AND DISCUSSION:

REEs Concentration of Soil Samples:

The distribution of REE in different Sites near the Paper mill in Manikpara (Fig.1) indicates that LREE are more abundant than the HREE.

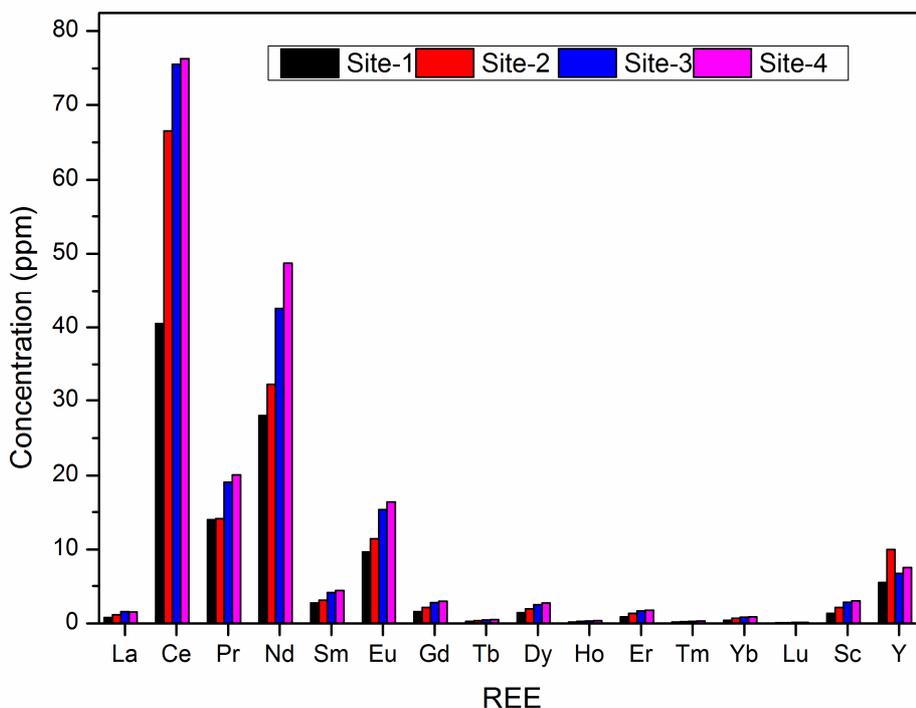


Fig.1. Distribution of REE in Different Sites from the Paper Mill Area.

As shown in Table.1, the average total content of REEs (\sum REE in ppm) of Site-4 was found to be the highest (187.555), followed by Site-3 (176.523), Site-2 (147.676) and the control Site (Site-1) (107.345). The average total LREEs of all the sites accounted for more than 87% of total REE content whereas the average total HREE were relatively rare (10%).

Among the individual REEs Ce is the most abundant of the whole REEs with a range of (40.498 - 76.292) ppm and accounted for more than 37% of the total REE content in all the sites followed by Nd (28.003-48.734) ppm. The value of Y in the Site-2 is 45%, 32% and 23% higher than the control Site, Site- 3, and Site- 4, respectively indicates that Y is significantly contributed for the \sum REE of Site-2.

Table.1 Mean REE concentration (ppm) in the different soils of different distance from the Paper mill

REE	Site-1 (Control site)	Site-2	Site-3	Site-4
139La	0.770	1.150	1.547	1.519
140Ce	40.498	66.494	75.558	76.292
141Pr	13.972	14.100	18.946	20.094
146Nd	28.003	32.308	42.550	48.734
147Sm	2.738	3.083	4.093	4.398
153Eu	9.641	11.417	15.315	16.311
157Gd	1.560	2.113	2.782	2.973
159Tb	0.245	0.353	0.451	0.503
163Dy	1.416	1.931	2.508	2.715
165Ho	0.181	0.257	0.326	0.351
166Er	0.889	1.348	1.653	1.766
169Tm	0.153	0.237	0.288	0.311
172Yb	0.427	0.678	0.805	0.860
175Lu	0.059	0.096	0.112	0.120
45Sc	1.328	2.137	2.810	3.012
89Y	5.464	9.973	6.779	7.598
∑ REE	107.345	147.676	176.523	187.555
∑ LREE	95.622	128.553	158.009	167.347
∑ HREE	11.722	19.123	18.514	20.207
∑ LREE/∑HREE	8.157372	6.722445	8.534339	8.281594
∑ LREE/∑ REE	0.890798	0.870507	0.895116	0.89226

The availability and distribution of REE in the soil are influenced by the type of soil and its content, mineral weathering, on geochemical and biological processes, pH of the soil, oxidation-reduction condition, rain, underground water²²⁻²⁵. The cumulative load of coal fly ash and bottom ash accumulated in the soil near the paper mill may contribute to increasing the REE content of the soil⁹. Soil nearby the paper mill may be contaminated with the organic matters like chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols, dibenzofuran, chlorinated hydrocarbon, etc. due to improperly disposed of the paper mill effluents²⁶⁻²⁸. These soil organic matters as they contain a large number of carboxyl groups, Phenolic hydroxyl groups, oxygen or other heteroatom binding sites are thought to easily retain the REEs in the soil through adsorption and/or chelation^{29,30}.

The complexation of the REE elements also involves coordination with various inorganic anionic species from the effluent and expressed as $REE^{3+} + yL^{n-} = REE-L_y^{(3-yn)}$ where L^{n-} is the ligand having n ionic charge and y is the stoichiometric coefficient. Effluent generated from the pulping unit of the paper mill in the form of black liquor may contain OH^- , CO_3^{2-} , S^{2-} , HSO_3^- which can easily be complexed with the REEs and thus retain in the soil³¹. The hard acid $LREE^{+3}$ can form more stable complex with the hard base like CO_3^{2-} present in the lime mud of the paper mill waste. $HREE^{+3}$ forms more stable complex with bicarbonate³²⁻³⁶ as $[REE(CO_3)]^+ + H_2O + CO_2 \rightleftharpoons [REE(HCO_3)_2]^+$. REEs in the soil may undergo hydrolysis at different pH as $REE^{+3} + nH_2O = REE$

$(OH)_n^{3-n} + H^+$ and stability of various hydrolytic products increases with the increasing atomic number³⁷. Continuous deposition of the lime mud from the paper mill may increase the carbonate mineral content of the soil. REE⁺³ s are easily incorporated into carbonate minerals through the isomorphic exchange for Ca⁺² in CaCO₃ lattice due to the similar ionic radius³⁸.

As the Site-4 is very close to the paper mill, the soil may be contaminated more with the organic and inorganic matters of the effluent as well as the coal fly ash compared to the other sites i.e. Site- 2, Site- 3 and the control Site. The increasing content of REEs in the soil close to the paper mill thereby, confirming the interaction of effluent from the paper mill with the REEs present in the original soil and in the coal fly ash (Fig.2). Thus, the increase in REE content in the soil due to the industrial activity are consistent with the previous findings^{39,40}.

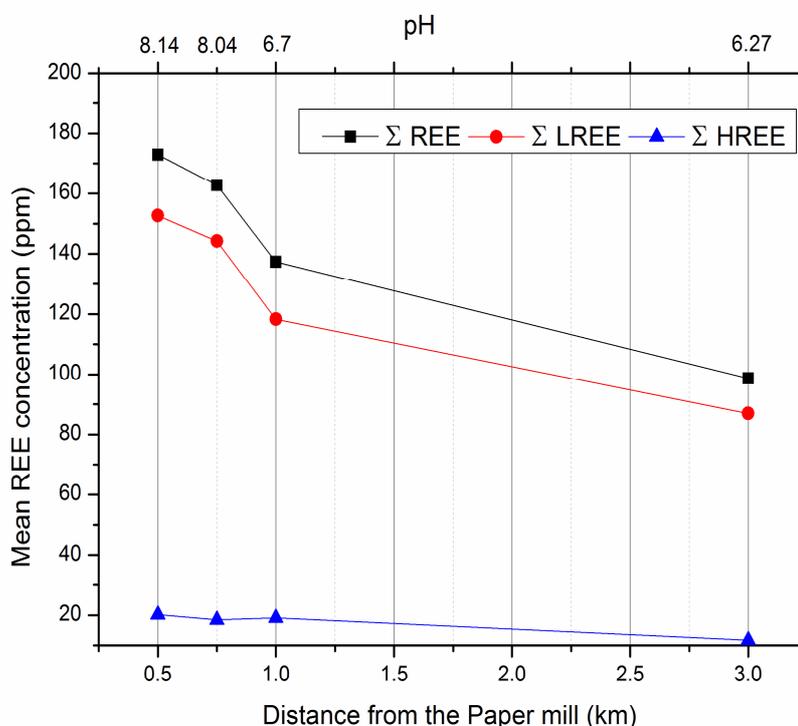


Fig.2 Distribution of ΣREE, ΣLREE, ΣHREE at Different Distance from the Paper mill.

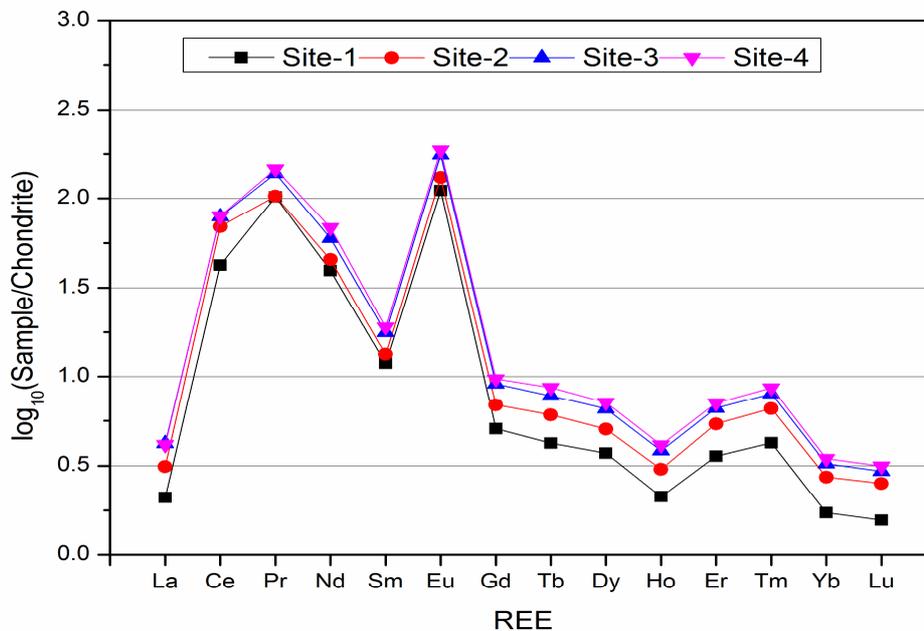
The Kaolinite clay mineral present in the soil of this area can adsorb the REEs by substitution for alkali or alkaline earth metal which adsorbed into the different layers of clay mineral⁴¹⁻⁴³. Laterite soil of this area contains secondary mineral Fe-Mn oxide and/or oxyhydroxides may scavenge the REEs in the soil⁴⁴⁻⁴⁸.

The average total content of REE (i.e. ΣREE) increases with increase in soil pH (as pH of the Site-1, 2, 3, 4 are 6.27, 6.7, 8.04, 8.14, respectively) which is also consistent with the previous findings^{49,50}. As under basic condition, the REEs adsorbed as inner-sphere complexes onto

the amphoteric sites at the edges of the particles (strong chemisorptions, variable pH dependent charge) whereas at acidic condition REEs adsorbed as outer-sphere complex onto the basal surfaces of Kaolinite clay mineral (weak physisorption related to permanent structural charge)⁵¹.

As shown in Table.1, \sum LREEs are increased by 1.75, 1.65, 1.36 times whereas the \sum HREEs are increased by 1.72, 1.63, 1.57 times in site-4, site-3 and site-2, respectively than the control site. \sum LREE/ \sum HREE values are varied from 6.7 to 8.5 suggesting that the LREEs are more abundant in these soils. The value of \sum LREE/ \sum HREE of site-2 is low (6.7) among all the samples as the concentration of Y is highest in site-2. With the soil development, the more mobile HREEs are depleted gradually due to their small sizes and the LREEs are enriched³⁹.

A chondrite-normalization plot is the logarithm of the normalized abundance of the REEs versus the atomic number of the REEs is depicted in Fig.3, used to study the distribution pattern of REE using the concentration⁵². From the figure, it is evident that the REE distributions are characterized by LREE-enrichment and HREE-depletion. The high value of \log_{10} (Sample/Chondrite) of site-4 than the other sites indicates more enrichment of REE in the soil. The equivalent distribution pattern of REE indicates the same type of chemical weathering of the parent mineral (probable feldspar) takes place. The fractionation between LREEs and HREEs may be attributed to the preferential sorption of LREEs onto the secondary mineral like clay mineral, Fe-Mn oxyhydroxides, Fe-oxides, and the preferred activation and/or leaching of HREEs⁵³.



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Fig.3. Chondrite Normalized Diagram Showing the Distribution Pattern of REEs of Different Soils of the Paper Mill Area.

The Europium anomaly (Eu / Eu*) and the Cerium anomaly (Ce/Ce*) was calculated as: $Eu / Eu^* = Eu_N / (Sm_N \times Gd_N)^{0.5}$, $Ce/Ce^* = 3Ce_N / (2La_N + Nd_N)$ where Eu_N , Sm_N , Gd_N , Ce_N , La_N , Nd_N implies the respective REE concentrations normalized to Upper Continental Crust (UCC) (Taylor and McLennan, 1981)⁵⁶. Positive Eu-anomaly in the soil matrix (14.2, 13.6, 13.8 & 13.7 for Site-1, 2, 3 & 4, respectively) was attributed to the preferential weathering of Feldspar minerals over the pedogenic timescale^{57,58}. When the primary mineral Feldspar crystallize and growth from magma in absence of dioxygen Eu^{+2} substitute into Ca^{+2} , Na^{+} or K^{+} sites⁵⁹. Adsorption of Eu on the Kaolinite clay mineral formed by the chemical weathering of the original rock feldspar may also originate the equivalent positive Eu anomaly of all the soil samples^{60,61}. The soils exhibit positive Ce- anomaly (2.9, 4, 3.4 & 3.1 for Site-1, 2, 3 & 4, respectively) are due to the low mobility of Ce(IV) as low solubility of cerianite(CeO_2) and strong interaction (via adsorption and/or coprecipitation) with the Fe and/or – Mn oxides present in the secondary minerals^{62,63}.

STATISTICAL ANALYSIS:

Pearson correlation analysis was performed⁶⁴ between all the REEs as the variables. The level of significance ($p \leq 0.05$ and $p \leq 0.01$) of multi-element correlation for soil samples was determined and the results are given in Table .2

Table: 2 Correlation-coefficient matrix between REES (N=16)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Sc	Y
La	1	.978**	.909*	.942*	.959**	.974**	.989**	.983**	.987**	.990**	.991**	.988**	.987**	.984**	.993**	0.456
Ce		1	0.815	.886*	.896*	.919*	.958*	.962**	.959**	.971**	.985**	.986**	.992**	.994**	.978**	0.633
Pr			1	.979**	.987**	.977**	.946*	.933*	.943*	.926*	.898*	.892*	0.874	0.863	.916*	0.102
Nd				1	.995**	.991**	.979**	.979**	.981**	.971**	.953*	.950*	.937*	.930*	.963**	0.284
Sm					1	.998**	.986**	.979**	.985**	.975**	.958*	.954*	.941*	.934*	.969**	0.262
Eu						1	.993**	.987**	.992**	.985**	.971**	.968**	.958*	.951*	.981**	0.306
Gd							1	.998**	.998**	.998**	.992**	.990**	.984**	.980**	.997**	0.412
Tb								1	.999**	.999**	.995**	.994**	.989**	.986**	.997**	0.452
Dy									1	.999**	.993**	.991**	.986**	.982**	.997**	0.423
Ho										1	.998**	.997**	.993**	.990**	.999**	0.463
Er											1	.998**	.999**	.997**	.999**	0.520
Tm												1	.999**	.998**	.998**	0.535
Yb													1	.998**	.995**	0.564
Lu														1	.993**	0.582
Sc															1	0.482
Y																1

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

The significant high positive correlation among the REEs indicates their similar chemical properties and common natural origin⁶⁵. The listed r values indicated the high degree of positive correlations and significant linear relation between various pairs of REEs, reflecting their

simultaneous release and identical source from the paper mill area, transport and accumulation in soil. The strong association among the elements indicates common sources and these metals have been derived from anthropogenic sources, especially the paper mill sewage system.

CONCLUSION:

Enrichment of REEs due to the improper disposal of untreated sewage along with Coal fly ash and bottom ash from the paper mill arises in the nearby soil. Chondrite-normalized REE distribution between the soils of different sites indicates LREE-enrichment and HREE-depletion. The total content of REE (Σ REE) is highest in site-4, which is closest to the paper mill followed by site-3, site-2 and site-1 (control site). Thus, the enrichment of REEs decreased with increasing distance from the paper mill. Positive Eu anomaly was found for all the sample soil. Further, studies are to be performed to monitor the mobility and bioavailability of REEs in the soil, to understand the bioaccumulation of REEs in plants in the affected soil and human exposure risk.

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