RARE ELEMENTS PATTERNS IN SOIL AROUND KADUNA REFINERY, KADUNA STATE, NIGERIA

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Abstract
Rare earth elements (REEs) are always found together in the crustal environment. This makes the group of elements a veritable tool as geochemical markers. The soil around the Kaduna Refinery was investigated for rare earth elements (REE) to evaluate the extent to which the rare earth elements patterns were distorted by the operations of the Refinery. Neutron Activation Analysis (NAA) of the samples revealed that five of these elements were determined among which, one (Lanthanum (La)) was a light rare earth element (LREE), three (Dysprosium (Dy), Yterbium (Yb), and Lutetium (Lu)) were heavy rare earth elements (HREE), and one Europium (Eu) was a middle rare earth element (MREE). For each sample, the chondrite-normalized $(REE)_{cn}$ (Haskin, 1984) values were determined which were plotted against their corresponding ionic radii. No distortions were observed in the patterns as the plots showed consistency with the general trend of the REE given by the $La/Lu)_{cn}$ ratio and exhibited both the Eu and Dy anomalies which are characteristic of upper plains and flood plains respectively.

Keywords: REE, Kaduna refinery, INAA

Introduction
Rare earth elements (REEs) belong to a group of 15 elements. All of these elements occur naturally in the continental crust except promethium. REEs are not actually rare (Šmuc *et al*., 2012), only that they exist in low density ores and are hard to extract and separate. REEs, because of their physico-chemical properties tend to stay together naturally and this explains their similar behaviour in the environment (Henderson, 1984; Hu *et al.,* 2006). There has been no report about the toxicity or otherwise of the rare earth elements (Hu *et al.,* 2006; Laveuf and Cornu, 2009); perhaps this accounts for the fact that very little attention has been paid to them. However, several reports (Hong *et al*., 2000; Ding *et al*., 2006; Hu *et al*., 2006) revealed highly elevated levels of some REEs (La, Ce, Sm, Eu, and Tb) in agricultural soils. The mobility characteristics of REEs constitute one of the most crucial factors to consider when evaluating the environmental impacts of the elements present in the soil. The soluble, exchangeable and the chelated REEs are however the only fractions that is bioavailable to plants.

Scientific investigations have also revealed that these elements are very vital in different fields of science and technology (Hanson, 1980; Henderson, 1984; Aubert *et al*., 2004; Han and Liu, 2006; Tyler, 2004; Willis and Johannesson, 2011). This revelation has brought about renewed interest in the search for REEs, especially to break the Chinese monopoly over the global market for this group of elements. For this reason, investment in the production of rare earth elements has surged recently (Chen, 2011; Charalampides *et al.,* 2015; Dutta *et al*., 2016).

Materials and Methods

Materials
NIRR-1 is a miniature Neutron Source Reactor (MNSR) and has a tank-in-pool structural configuration with a nominal rating of 31kW and a neutron flux of 10^{12} n/cm^2/s. The reactor is fuelled by highly enriched uranium. Light water serves a dual purpose of the moderator and by the natural convection process as the coolant. The fuel assembly has beryllium as the reflector. It is specifically designed for neutron activation analysis (NAA), hence, it is capable of being used for analysis of trace, minor, and major elements in different sample matrices.

The neutron flux parameters of miniature neutron source reactors are known to be very stable, thus lending it to the use of semi-absolute NAA method (Akaho and Nyarko, 2002; Jonah *et al,* 2005). NIRR-1 was critical in 2004 and has been used for the analysis of geological and biological samples (Jonah *et al*, 2006).

The Study Area
Kaduna Refining and Petrochemical Company (KRPC) and its environs lies in the southern part of Kaduna city, occupying an area between latitude 10^o, 24' 22.32" - 10^o 25' 18.8" N and longitude 7^o, 29' 9.6" - 7^o 29' 55.2" E**.** Among the host communities of the refinery Complex is Rido village in the southern part of Kaduna metropolitan city. Apart from the petroleum refining, processing and oil-related activities, the predominant occupation of the inhabitants of the area is farming.

Plate I: The study area showing sample locations

Sampling
Near surface soil samples were collected from depths of 0-20 cm from farmland along the effluents discharge track and other farmland surrounding the refinery complex. These samples which were collected using a core sampler were air-dried at ambient temperature and stored in polyethylene bags which were thoroughly washed prior to sampling to avoid cross-contamination to ensure uniform irradiation. While sampling, attention was given to farm lands where the river water mixed with the effluents was being used for irrigation. Soil samples were also collected from the sludge pit where wastes in form of oil were dumped.

Sample Preparation

The dried samples were transferred to the laboratory at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, Nigeria and crushed into near-uniform particle size powder and each was weighed into a pre-cleaned polyethylene bag and sealed with a hot soldering iron into a 7cm^3 rabbit capsule. Thereafter, the sample capsules were packaged into bigger vials in preparation for irradiation.

Sample Irradiation

Irradiation is simply the exposure of a sample to nuclear radiation. The vials containing the rabbit capsules were sent to the reactor irradiation sites using the pneumatic transfer system called the rabbit system. The irradiation was done using the 31 kW tank-in-pool Miniature Neutron Source Reactor (the Nigeria Research Reactor-One, also called NIRR-1) with a neutron flux of 10^{11} n/cm^2/s. The software, WINSPAN was used for the spectrum analysis. Table 1 gives the details of the irradiation and counting regimes used in this work. Gamma energy lines free of interference were used for peak integration and are shown in Table 2 with other nuclear data.

After the counting was completed, the waste samples (which became radioactive due to the irradiation) could be of radiological concern; hence, they were disposed based on acceptable procedures in line with international best practices by designated Officers of the Radioactive Waste Management Section of the Centre for Energy Research and Training, Ahmadu Bello University, Zaria.

Table 1:Typical irradiation and counting schemes used for this study

Neutron flux/irradiation channel	Procedure	$T_{irradiation}$	T_{decay}	$T_{measuring}$	Activation products
$1x10^{11}$n/cm^2 s /outer irradiation	S1	2 min	2-15 min	10min	^{28}Al, ^{27}Mg, ^{51}Ti, ^{52}V, ^{66}Cu
channels (B4, A2)	S2	2 min	3-4h	10min	^{165}Dy, ^{152m}Eu
5×10^{11}n/cm^{2}s /inner	L1	6h	4-5d	30min	^{140}La
irradiation Channels (B1, B2, B3, and A1)	L2	6h	10-15d	60min	^{152}Eu, ^{177}Lu,^{175}Yb, ^{181}Hf.

Table 2: Nuclear data for the elements of interest used for this study

Target Isotope	Product isotope (n,γ)	Half-life	Gamma energy (keV)
^{139}La	^{140}La	40.30 h	1596.21
^{151}Eu	^{152}Eu	13.30 y	1408.50
^{164}Dy	^{165}Dy	2.33 h	94.70
^{174}Yb	^{175}Yb	4.19 d	396.33
^{176}Lu	^{177}Lu	6.71 d	208.36

Results and Discussion

The distribution patterns of the rare earth elements (REEs) around the Kaduna Refining and Petrochemical Company have been presented in Figures 1 – 3. The samples were randomly grouped into three with group membership as indicated (S01, S02, S03, S05, and S06 for group 1; S04, S07, S08, S10, and S11 for group 2; and S09, S12, S13, S14, and S15 for group 3) for the purpose of clarity of patterns, and plots were generated for each group.

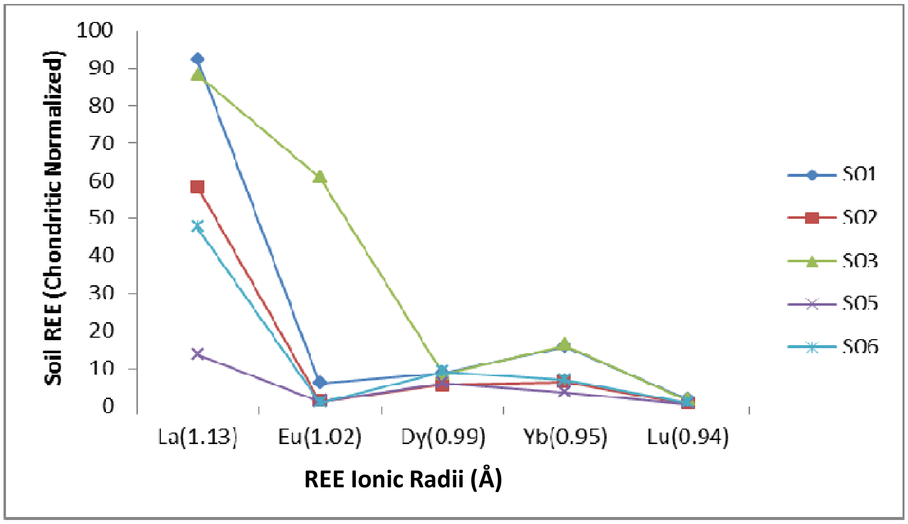

Figure 1: Rare earth plots for samplesS01, S02, S03, S05, and S06

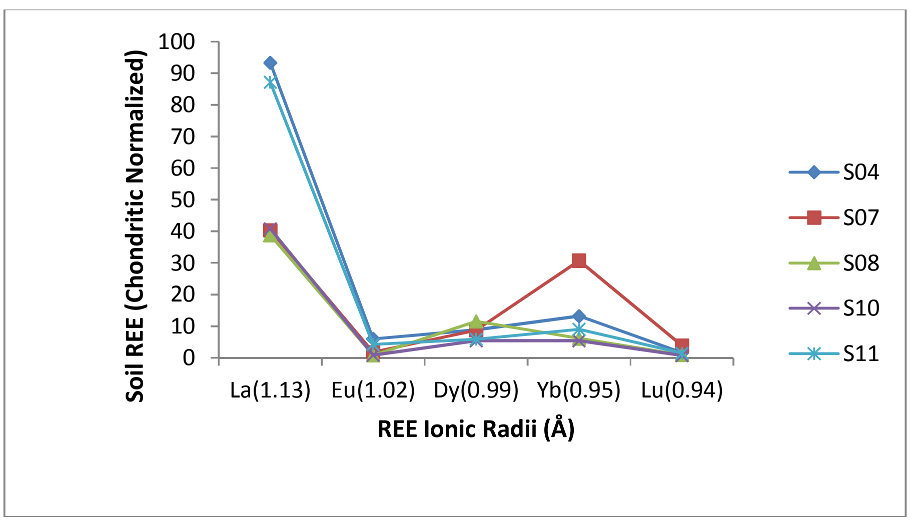

Figure 2: Rare earth plots for samples S04, S07, S08, S10, and S1

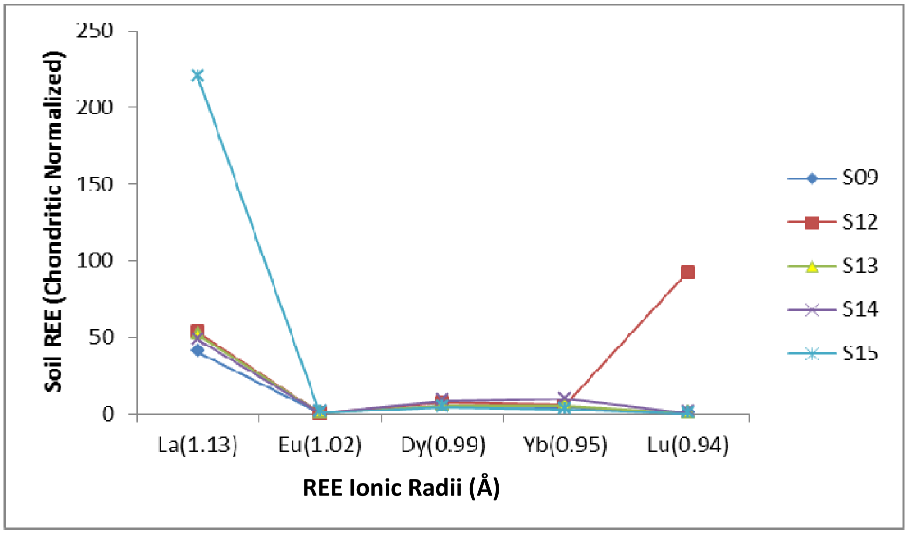

Figure 3: Rare earth plots for samplesR S09, S12, S13, S14, and S15

Results of analysis revealed that five rare earth elements were identified in soil around the Kaduna refinery. Among these, one (La) was a light rare earth element (LREE), three (Dy, Yb, Lu) were heavy rare earth elements (HREE), while one (Eu) was a middle rare earth element (MREE). For each sample, the chondrite-normalized $(REE)_{cn}$ values were determined using Haskin (1984) chondritic values. $(REE)_{cn}$ values for each sample were plotted against their corresponding ionic radii as shown in Figures 1 – 3. Most of these patterns were identical, confirming similarities in chemical behaviours of the elements, while some are not (S03 and S12), indicating some anomalies in the patterns. The general trend of the REE for each sample is a measure of the slope of the $(REE)_{cn}$ plots given by the $(La/Lu)_{cn}$ ratio (Ewa *et al*., 1996).

Apart from sample S12, all samples analysed showed fairly high to extremely high ratios, attaining an outrageous value of 440.7 in sample S15 taken from the refinery sludge pit. The plots are consistent with REE trends. All the soils investigated (except of S03 which showed Dy anomaly) showed significant and negative Eu anomalies that correspond to the deep Eu depression as could be seen on the chondrite – normalized patterns (Figures 1 – 3), while S12 showed a substantial enrichment of Lu. The negative anomalies were characteristic of Eu distribution in the soil. A number of factors such as the sub-tropical climate, soil secondary minerals, and soil physicochemical properties were responsible for the negative Eu anomaly. The Dy anomaly on the other hand exhibited the characteristic features of REE elements in flood plains similar in nature to the fadama soil where some samples were collected.

Conclusion

The chondrite - normalized REE patterns observed in the soil around the refinery were similar having a very clear negative europium anomaly. Fractionation occurred between the light rare earth elements (LREEs) and the heavy rare earth elements (HREEs) in different soil types. This could be attributed to the higher absorptive affinity of LREEs to soil mineral lattice than that of the HREEs. The active geochemical processes in the soil in addition to the effects of soil minerals were probably responsible for the negative europium anomaly.

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