



## Geochemical characteristics of rare earth elements in different types of soil: A chemometric approach



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### HIGHLIGHTS

- REEs concentration and physical parameters were studied in soils from different regions.
- Concentration of REEs decreases by moving from surface soil to deeper soil.
- PCA revealed that soil samples from different locations are separated into four clusters.
- PH and EC are dominating factors in separating industrial soil from other regions.

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### ABSTRACT

Rare earth elements (REEs) are becoming significant due to their huge applications in many industries, large-scale mining and refining activities. Increasing usage of such metals pose negative environmental impacts. In this research ICP-MS has been used to analyze soil samples collected from former ex-mining areas in the depths of 0–20 cm, 21–40 cm, and 41–60 cm of residential, mining, natural, and industrial areas of Perak. Principal component analysis (PCA) revealed that soil samples taken from different mining, industrial, residential, and natural areas are separated into four clusters. It was observed that REEs were abundant in most of the samples from mining areas. Concentration of the rare elements decrease in general as we move from surface soil to deeper soils.

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### 1. Introduction

Rare earth elements (REEs) are a group of seventeen elements with identical physical and chemical properties and similar behavior in the environment (Hu et al., 2006). REEs are not rare in their true sense from the geochemical point of view but are abundant in the earth crust after Cu, Zn, and Pb (Wang et al., 1998). REEs have been categorized into light rare earth elements (LREEs) and heavy rare earth elements (HREEs), from lanthanum to

samarium, and europium to lutetium, respectively depending on the atomic number (Khan et al., 2016). In this recent decade, due to increasing demand, REEs are being used in high technology, agriculture, industries, and engineering. Global demand is estimated to increase 120,000 tons to 150,766 tons from 2014 to 2020 (Kumari et al., 2015). REEs have been used in different fields of earth sciences such as geology, hydrology, and geochemistry (Han and Liu, 2007).

Mining and rejects extractions has been one of the most important factors contributing to REEs pollution into the environment such as soil, water, air, and humans (Hirano and Suzuki, 1996; Agudelo-Castañeda et al., 2016; Civeira et al., 2016a, 2016b; Dalmora et al., 2016; Meryem et al., 2016; Saikia et al., 2016;

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Schneider et al., 2016; Sehn et al., 2016).

Some research done on this, is nano metric and ultrafine sediments dumping into the rivers and lakes effecting the ecosystem and quality of water by adding hazardous elements. Abandoned acid mine drainage from copper mines acts as chief source of pollutants. Analysis of coal samples and fly ash showed the presence of minerals in its low grade form. Geochemistry of burning coal cleaning rejects (BCCRs) and anthropogenic impacts represents environmental concerns especially with soil, water, atmosphere and sediments. Trace and heavy metals present in the dust particles around basalts mining zone and hazardous elements (HEs) from abandoned coal mines, agricultural activities, urban discharges, dye industry and leisure zones cause major pollution. Different agricultural minerals also pose negative health impacts (Sanchís et al., 2015; Sindelar et al., 2015; Tezza et al., 2015; Wilcox et al., 2015; Rodriguez-Iruretagoiena et al., 2016).

REEs are more important for researchers in environmental sciences as are good indicators for soil processes (Tyler, 2004). Average concentrations of REEs in earth crust ranged from 150 ppm to 200 ppm (Long et al., 2010) and in soil  $4.67 \times 10^3 \text{ mg kg}^{-1}$  (Barnard and Halbig, 1985; Liang et al., 2014). Lots of previous studies indicate high concentration of most of the REEs in agricultural, industrial, and urban areas (Yoshida et al., 1998; Hong et al., 2000; Hu et al., 2006; Meryem et al., 2016). Meryem et al. (2016) indicated high levels of La, Ce, and Nd in the agricultural soils of smelting and mining areas in Hezhang, China. Total REEs concentration in smelting and mining areas were  $277.06 \text{ mg kg}^{-1}$  and  $177.79 \text{ mg kg}^{-1}$  respectively. Another study reported by Smuc et al. (2012) illustrated low concentrations of La, Ce, Pr, Nd, and Sm in paddy soil and rice of eastern Macedonia.

REEs have been found less in mineable ore deposits but widely distributed in the soils. Kumari et al. (2015) and Wiche and Heilmeyer (2016) reported high values for La and Nd in herbs than in grasses and pointed out that bioavailability of REEs depends largely on soil properties. Previous studies reported the leaching of La from acid sulfate soils from oxidized topsoil which decrease with less acidic subsoil (Åström, 2001; Welch et al., 2007; Gröger et al., 2011). REEs associated with major minerals such as monazite, xenotime, bastnasite, and bauxite ores have been found to be rich with REEs in some studies (Boni et al., 2013; Haniççi, 2013; Radusinović et al., 2016).

Perak is located on the west coast of peninsular Malaysia. Kinta Valley is located in the middle of Perak with tin and alluvial deposits. This area is considered as a mining heritage because of its glorious mining activities from 1884 to 1895 (Ahmad and Jones, 2013). Kinta district is nominated as the area with highest hectare (47,614 ha, 58.2%) of ex-mining land (Osman and Siong, 2012).

This study aims to map soil samples from former ex-mining areas of Perak according to REE concentration and physical parameters.

## 2. Material and method

### 2.1. Sampling and sample preparation

Soil samples have been collected from mining, residential, natural, and industrial regions in west of Perak including Lahat, Menglembu, Kinta Valley, Batu Gajah, and Kampong Sri located at the latitude  $04^\circ 51' \text{ N}$  and longitude  $101^\circ 02' \text{ E}$ . Samples from these areas were collected from three different depths as surface soil (0–20 cm), sub soil (21–40 cm) and deeper soil (41–60 cm) using auger. Then the samples were stored in polyethylene bags, kept in cool box, and transferred to laboratory for further analysis. The samples were air dried, grounded and sieved through 2 mm sieve to obtain homogeneous particle size. Soil samples were digested in nitric acid and hydrogen peroxide using microwave digester CEM-Mars Xpress (CEM cooperation, Matthews, NC.U.S.A). For this, 0.1 gr of soil sample was digested in 2 ml of supra pure nitric acid 60% Merck, Germany and 1 ml of supra pure hydrogen peroxide 30% Merck, Germany (Gholami et al., 2016). The microwave digestion system followed the program which was power to temperature mode starting with 300 W and holding time for 2 min, and rising to 600 W and holding 10 min, and afterwards reducing to 300 W for 5 min leaving the microwave to rest for 5 min.

### 2.2. Sample analysis

Soil samples in this research were analyzed using ICP-MS 7500ce Agilent. All calibration standards were prepared from the Agilent multi element calibration standard 8500-6944 containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, and Yb in 5%  $\text{HNO}_3$ .

All the standards were diluted by ultra-pure water for determining the concentration of elements in the digested soil samples. For linear calibration plot, five standards namely 10, 30, 50, 75, and 100  $\text{ng ml}^{-1}$  were prepared. In the calibration plot, the correlation coefficient was from 0.9994 to 0.9996 depending on the element. Similar analytical procedures were previously reported (Arenas-Lago et al., 2013; Cerqueira et al., 2013; Hower et al., 2013a, 2013b; Kronbauer et al., 2013; Oliveira et al., 2013; Ribeiro et al., 2013a, 2013b; Sanchís et al., 2013; Silva et al., 2013a, 2013b; Arenas-Lago et al., 2014; Cutruneo et al., 2014; Dias et al., 2014; Garcia et al., 2014; Martinello et al., 2014; Oliveira et al., 2014; Osório et al., 2014; Pérez et al., 2014; Saikia et al., 2014).

**Table 1**  
Quality control parameters for SRM 2586.

| Elements | Obtained ( $\text{mg kg}^{-1}$ ) | Certified ( $\text{mg kg}^{-1}$ ) | LOD ( $\mu\text{g L}^{-1}$ ) | LOQ ( $\mu\text{g L}^{-1}$ ) | CV (%) | Recovery % |
|----------|----------------------------------|-----------------------------------|------------------------------|------------------------------|--------|------------|
| Y        | $22.0 \pm 9.5^c$                 | $21.0^a$                          | 0.0004                       | 0.001                        | 0.43   | 97.62      |
| Ce       | $56.0 \pm 9.5^c$                 | $58.0 \pm 8.0^b$                  | 0.0020                       | 0.005                        | 0.17   | 96.55      |
| Dy       | $5.3 \pm 1.2^c$                  | $5.4^a$                           | 0.0010                       | 0.002                        | 0.23   | 98.00      |
| Sc       | $24.6 \pm 12.8^c$                | $24.0^a$                          | 0.0400                       | 0.130                        | 0.52   | 95.83      |
| Tm       | $0.50 \pm 0.07^c$                | $0.50^a$                          | 0.0002                       | 0.001                        | 0.14   | 100.00     |
| La       | $29.0 \pm 5.1^c$                 | $29.7 \pm 4.8^b$                  | 0.0004                       | 0.002                        | 0.17   | 97.64      |
| Tb       | $1.10 \pm 0.28^c$                | $0.90^a$                          | 0.0010                       | 0.002                        | 0.25   | 94.00      |
| Gd       | $6.03 \pm 2.90^c$                | $5.80^a$                          | 0.0020                       | 0.007                        | 0.48   | 99.13      |
| Er       | $3.70 \pm 0.25^c$                | $3.30^a$                          | 0.0010                       | 0.003                        | 0.07   | 93.94      |
| Yb       | $2.62 \pm 0.73^c$                | $2.64 \pm 0.51^b$                 | 0.0060                       | 0.019                        | 0.28   | 96.00      |

<sup>c</sup>CV= Coefficient of variation, LOD = Limit of detection, LOQ = Limit of quantification.

<sup>a</sup> The certified values are calculated from a single method or a mean of two method.

<sup>b</sup> The certified values are calculated based in two or more analysis and reported as mean  $\pm$  SD.

<sup>c</sup> All the obtained values are based on three observations and reported as mean  $\pm$  SD.

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