



# Rare earth elements profile in a cultivated and non-cultivated soil determined by laser ablation-inductively coupled plasma mass spectrometry



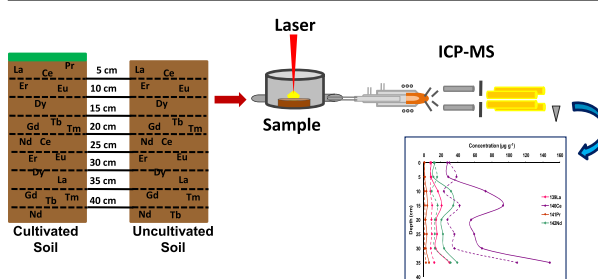
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## HIGHLIGHTS

- Fertilizers that contain REE in their composition can contaminate soil and water.
- The concentration of the REE is higher in the cultivated soil.
- REE increases from the surface to deeper layers of the soil.
- LA-ICP-MS allows direct analysis of solid samples.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Rare earth elements (REEs) have several applications but the effects on environment are not well known. Therefore, the aim of this work is to establish a method for direct solid sample analysis by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) to evaluate the concentration and distribution of REEs in cultivated and non-cultivated soil. Samples were collected in two areas to 40 cm of depth. The LA-ICP-MS method is easy to be implemented and the sample treatment is very fast comprising only its drying, grinding and pressing as a pellet. The accuracy of the method was evaluated by using a certified reference material (BCR 667 – Estuarine Sediment, Institute for Reference Materials and Measurements (IRMM)) where good agreement with the certified values was obtained. Analyte recovery at two levels of concentration (2.5 and 15.0  $\mu\text{g g}^{-1}$ ) was also performed and recoveries in the range of 85%–120% were achieved, values that are acceptable for LA-ICP-MS analysis. In general, the concentration of the REEs is higher in the cultivated soil and increased from the surface to deeper layers, which can be a consequence of fertilizer application.

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## 1. Introduction

Rare earth elements (REEs) belongs the group *f* and comprise 17

elements. Information about the contents of REEs in several types of materials is important in geochemical, biochemical and environmental studies. Nowadays, there is an extensive application of these elements in several industrial areas due to its electronic, optical, magnetic and catalytic characteristics. REEs are present in smartphones, rechargeable batteries, jet engines, fluorescent lamps, automotive catalysts, and catalyst for crude petroleum

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cracking and imaging contrast in magnetic resonance (Gonzalez et al., 2014).

China is one of the greatest producer and consumer of REEs and the country was the first (in 1972) to use these elements as fertilizers. Studies, mainly in China, show that REEs when present in certain concentrations improves seed germination, growing, appearance and quality of plants (Thomas et al., 2014). However, the information on the influence and toxicity of REEs on plant development remain contradictory and unclear. There is no accurate information on the use of REEs as fertilizer, but the treated area with rare earths in China constantly increased from a minor area of 1330 ha in 1980 to about 16 million ha in 1995. It means that by 1995, the treated surface with fertilizers containing REEs was 160,000 km<sup>2</sup> (Pang et al., 2002; Tyler, 2004; Charalampides and Vatalis, 2015).

The use of fertilizers, mining activities and incorrect disposal of devices that contain REEs in their composition are the main anthropogenic sources of these elements and can contaminate soil and water. However, little is known about beneficial or toxic effects on health and environment (Rim, 2016). Therefore, there is an increasing concern and interest about the environmental monitoring of REEs. Accurate and precise analytical methods are necessary to monitor small changes of the concentration of one element in environmental matrixes, such as water, sediment and soil (Fiket et al., 2016; Kratii et al., 2017; Wysocka and Vassileva, 2017). Due to the relatively low concentration of REEs in soil, few analytical techniques are able to detect these elements. The most common techniques used for REEs determination in soil include instrumental neutron activation analysis (INAA), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) (Kramer et al., 2002; Ardini et al., 2010). INAA is an absolute technique and needs low amounts of sample for analysis. However, it is a time-consuming technique and requires a reactor for neutron generation, which makes its application difficult for routine analysis (de Corte and de Wispelaere, 2004; El-Taher, 2010). ICP-OES is more convenient for multi-elemental determinations, but the limit of detection (LOD) is not sufficiently low to detect some of the REEs in soil (Bentlin and Pozebon, 2010). Perhaps, ICP-MS is currently the most reliable technique for REEs determination because of its multi-element capability and mainly due to the very low LOD achieved. However, one of main inconvenience in ICP-OES and ICP-MS techniques is the sample preparation when operated in conventional mode with sample introduction by pneumatic nebulization (Limbeck et al., 2017). In this case, the sample must be in solution. This can be achieved by different procedures, such as acid decomposition or alkaline fusion. However, for soil decomposition high amounts of HNO<sub>3</sub>, HCl, HF and others reagents are necessary. The acid decomposition can be accelerated and improved by submitting the sample to high temperatures and pressures. Usually, this can be achieved in closed systems and by using microwave energy (sample decomposition in microwave ovens), which can reduce the time of decomposition but at a high cost. Besides, when HF is used, REE form insoluble compounds. In this case, it is necessary to treat the final solution with boric acid (Bentlin and Pozebon, 2010; Fiket et al., 2016) to solubilize the precipitate. Soil can also be decomposed by alkaline fusion. However, it is well known that sample preparation by fusion can result in a risk of contamination, losses of elements by volatilization and can lead to a final solution with high salt content. Solutions with high salt content are also not favourable for analysis by ICP-MS due to salt deposition on the interface, changes in plasma characteristics and potential to induce space/charge effects. In addition, safety precautions must be taken in fusion procedures and they can take some minutes to many hours under high temperatures (Bayon

et al., 2008; Chand and Prasad, 2013).

A good alternative to sample decomposition is direct solid sample analysis. Electrothermal vaporization (ETV) and laser ablation (LA) are frequently coupled to ICP for direct solid sample analysis. Characteristics of these sample introduction systems include no decomposition of the sample, improvement in the LOD, the use of small sample amounts and microanalysis (Barth et al., 1997; Kaczala et al., 2015; Mello et al., 2015; Pozebon et al., 2017). In particular, the use of LA-ICP-MS increased in different fields of application because it combines high sensitivity, multi-element analysis capability, good spatial resolution and allows direct analysis of solid samples (Pozebon et al., 2014, 2017). Analysis by LA-ICP-MS requires the use of only a few mg of sample, and can in general be analyzed directly or after pressing as a pellet when the sample is in powder form. The amount ablated by each laser pulse is in the order of pg to ng. However, to obtain quantitative information from LA-ICP-MS is still a challenge, mainly as a consequence of elemental fractionation effects from the sample ablation, aerosol transport and element ionization by the plasma (ICP). Plasma stability can also be affected by loading the ICP with excessive amount of sample matrix. Due to these effects, different strategies have been used for analyte quantification in geological, biological, botanical and other materials (Pozebon et al., 2014, 2017; Nunes et al., 2016; Pozebon et al., 2017; Voss et al., 2017). In some cases, the calibration curve is prepared with certified reference material (CRM). However, the number of CRM is limited or the element concentration is not appropriate to construct a calibration curve. Therefore, another way is to prepare the standards in the laboratory. In general, matrix-matched standards are used and usually the preparation consists of pressing a powdered sample as a pellet. Binders and elements used as internal standards (IS) are usually added to the powder before pellet formation. Internal standards are used to overcome non-spectral interferences in the analysis such as differences in the laser interaction with the sample, vapour transport effects and fractionation effects. The choice of IS, is challenging and it is necessary to consider some aspects for satisfactory correction. The characteristics for an ideal IS includes the homogeneous distribution of the IS in samples and standards, the absence of spectral interference on the IS, similarity of IS and analyte behaviour in the plasma (mainly its ionization characteristics) and similarity of m/z (Durrant, 1999; Konz et al., 2013; Bauer and Limbeck, 2015).

In this work we developed a method for direct soil sample analysis using the LA-ICP-MS technique to investigate the distribution of REEs in soil from areas with and without agricultural activity. The study is focused to determine the concentration of REEs in different layers of soil sampled in an area where agricultural activities has been constant for at least 20 years with soya and wheat plantations against another area never used for agricultural or other activities.

## 2. Materials and methods

### 2.1. Reagents and standards

Concentrated HNO<sub>3</sub> (65% m m<sup>-1</sup>, Merck, Germany) and HCl (37% m m<sup>-1</sup>, Merck, Germany) were purified in a sub-boiling system (Milestone, Model Duopur, Italy) and used to prepare solutions. Ultrapure water (resistivity of 18 MΩ cm) was obtained by a Milli-Q system (Millipore corp., USA) and used for material cleaning and solution preparation. Multi-elemental reference solution containing 10 mg L<sup>-1</sup> REEs (CLMS-1, Multi-element solution –Spex Certi-Prep, USA) was used to prepare the matrix-matched calibration standards. A mono-elemental 10 mg L<sup>-1</sup> Au solution (Merck) was used as IS. Certified reference materials from Community Bureau of

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