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Rare earths and trace elements contents in leaves: A new indicator of the composition of atmospheric dust

P. Censi [a, *], F. Cibella [b], E.E. Falcone [a], G. Cuttitta [b], F. Saiano [c], C. Inguaggiato [a], V. Latteo [b]

[a] Department of Earth and Marine Sciences, University of Palermo, Via Archirafi, 36, 90123 Palermo, Italy
[b] IBIM - CNR, Via U. La Malfa, 153, 90146 Palermo, Italy
[c] SAF Department, University of Palermo, Viale delle Scienze, ED. 4, 90128 Palermo, Italy

HIGHLIGHTS

- Leaves composition of studied plants is driven by atmospheric particulate.
- Normalized REE patterns discriminate among sources of atmospheric dust.
- Normalized REE patterns discriminate between soil- and air-borne metal fluxes.

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ABSTRACT

The relationship between the trace element distribution in atmospheric particles and leaves of some exposed plants in the environment was recently demonstrated. This indication would suggest that the trace element analysis of leaves in these plants could provide information about the composition, nature and origin of the atmospheric dust dispersed in the environment. In order to corroborate this hypothesis, the distribution of trace elements and Rare Earths were studied in leaves of some endemic plants, in the atmospheric fallout and in soils of rural, urban and industrial ecosystems in Sicily. These elements have been chosen to discriminate the source and nature of different source on atmospheric dust and the larger capability of the composition of the latter materials to influence the metal ion distribution in leaves of studied plants rather than the soil composition. These evidences are related to the recognition both of positive La anomaly and trace element enrichments in studied leaves and to their particular V/Th and Co/Ni signature. On the other hand, some particular normalised REE features recognised in leaves suggest that a limited contribution to the REE budget in studied leaves is provided by the REE migration from roots.

1. Introduction

The environmental status and its compliance to natural conditions is a consequence of interactions among lithosphere, hydrosphere, biosphere, atmosphere and anthroposphere. As a consequence, minor and trace metal contents in plants represent a useful proxy of the environmental quality. The latter assessment requires the knowledge of the extent of metal ions migrations from soil through the rhizosphere and their transport by metabolic fluids in plants. On the other hand, several researches demonstrate that also leaves can trap metals leached from atmospheric dust particles (Schulze et al., 1982; Lohr and Pearson-Mims, 1996; Tomašević et al., 2004; Pallardy, 2008) and the importance of atmospheric input in the biogeochemical cycling of heavy metals was reviewed by Bargagli (1998). Therefore, the metal accumulation in plants can mirror both the soil and air quality contributing to depict a more complete scenario of the environmental status.

Nowadays, these latter studies have been limited to the investigation of the leaves contamination induced by the accumulation of minor and trace constituents with a larger environmental echo and other elements as lanthanides and yttrium (hereafter defined Rare Earths, REE) have been not studied although widely used in several technological devices (Du and Graedel, 2011). The REE content in plants was widely studied to investigate the bioaccumulation of these elements (Reimann and De Caritat, 2000, 2005; Tyler, 2004; Sucharovà et al., 2012; Reimann et al., 2015

* Corresponding author.
E-mail address: paolo.censi@unipa.it (P. Censi).

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and references cited) but limited indications about the REE fractionation in plants during metal ions migration from roots to aerial plant portions have been collected (Miao et al., 2011; Yu et al., 2007; Censi et al., 2014).

As a consequence, the aim of this study is to investigate the REE behaviour in plant leaves recognising if their content and distribution are influenced by the composition of atmospheric fallout or are simply related to the ion metal migration from soils. This information is suitable to play a key role during environmental analyses where leaves of endemic plants in given area can represent low-cost devices for collection of atmospheric particles in the ecosystem and the geochemical REE features of atmospheric particulates can be easily exploited to recognise effects of anthropogenic contamination in atmospheric fallout particles. Therefore, the REE distribution was studied in leaves of *Lobularia maritima, Malva sylvestris, Mercurialis annua, Senecium vulgaris and Solanum nigrum* species collected in several Sicilian area where different lithogenic background and anthropogenic signatures both under urban and industrial pressure occur. These plants have been selected for the different features of their leaves in order to test if the latter character can influence the recognition of the geochemical evidences of anthropogenic-lithogenic signatures. The REE study is coupled to V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Ba, Th and U investigation in order to exploit these metal ions as useful biological indicators of air quality. To achieve to these results this research is focused on the recognition of the geochemical behaviour of REE and related trace element distributions in selected plant leaves exposed to different air contamination levels.

2. Materials and methods

Investigated plants have been collected in several Sicilian sites representative of rural, industrial and urban environment in order to investigate a wide range of effects of the anthropic pressure on the air quality. The investigated plants can be commonly found in urban areas, along roads, streets and highways in Sicily. As reported in Fig. 1, the sampling sites are located at about 800 m height in the southern slope of the Appennino-Maghrebide chain

Fig. 1. Geographic sketch map of studied sites. The enlarged map depicts Palermo and the gradient filling represents the most urbanised area.

(Petralia site), in the southern slope of Etna volcano at about 500 m height (Pedara site), close to a large industrial pole with oil refinery and power plants in the eastern coast of Sicily (Priolo site), downtown Palermo (PA-3) and in the suburbs (PA-1 and 2). Both Petralia and Pedara should represent low anthropised sites with different lithogenic background characters: sedimentary carbonatic the former and eruptive with frequent delivery of aerosol particles from the volcanic activity of Mt. Etna the latter (Calabrese et al., 2011). Ten specimens for each plant species were collected in the investigated sites and only leaves from each specimen were used for geochemical analyses. After the leaf collection from the plants in the field, leaves were stored in clean paper bags, closed in polyethylene bags and brought to the lab. Here leaves were stored in −80 °C freezer up to sample manipulation for chemical analyses. After storage in freezer, each plastic bag containing leaf samples was put at room temperature in a laminar flow bench. Leaves were put into a plastic beaker (500 ml in volume) and ultrapure water obtained by an EASY pure II purification system (Thermo, Italy) was added. Each beaker was treated ultrasonically for 10 min. After this treatment, leaves were removed from the solution, rinsed with ultrapure water and stored for further investigations. As follows, water cleaned leaves were washed in depth using a 0.01 M solution of H_2Na_2ETDA (AnalaR NORMALPUR®, VWR) at pH = 4.5 in order to remove any trapped particles onto the leaf surface and also to leach metals scavenged therein. The real removal of dust particles from leaf surfaces has been observed with a binocular microscope. After cleaning procedures, leaf samples were dried at 110 °C, weighed obtaining an aliquot close to 0.5 g, ground in an agate mortar, completely homogenised and stored in a Teflon PFA™ vessel. Here, a 9.0 ml of 2:1 v/v mixture of HNO_3 (65% w/w): H_2O_2 (30% w/w) was added; the container sealed and put in the microwave-assisted oven (CEM MARS 5 device).

The dust suspension obtained from the cleaning procedures of leaves was collected onto a membrane filter (Millipore™ manifold filter diameter 47 mm, pore size 0.45 μm) after the removal of leaves from the container. Dust particles were digested with 10 ml of $HClO_4$ - HNO_3 - HF solution in a Teflon PFA™ vessel sealed and put in the microwave-assisted oven (Alaimo and Censi, 1992; Ruberti et al., 2002).

Investigated soils were collected immediately around the plant roots, about 10–15 cm depth. Each soil sample was treated to extract the labile metal ion fraction in order to simulate the natural capability of the plant rhizosphere to extract metals from the soil. This extraction was carried out by treatment with DTPA at pH 5 (Ehlken and Kirchner, 2002; Ehlers and Luthy, 2003; Feng et al., 2005). Each mineralised solution was analysed with a quadrupole inductively-coupled plasma mass spectrometry (Q-ICP-MS, AGILENT 7500 series).

All chemicals used during lab manipulations were of ultrapure grade. Nitric acid 65% (w/w), ammonia solution and HCl were purchased from VWR International. Working standard solutions for each studied element were prepared on a daily basis by stepwise dilution of the multi-element stock standard solution DBH, Merck or CPI International (1000 ± 5 mg l^{-1}) in an HCl 1 mol l^{-1} medium. All labware were in polyethylene, polypropylene or in Teflon and the calibration of all volumetric equipment was verified. A calibrated E42-B balance (Gibertini, Italy) was used to weight all samples and standards. pH measurements were carried out with HI 991300 pH-meter (Hanna Instruments, Italy).

The assessment of the analytical precision of analyses carried out was assessed treating several aliquots of standard reference material (SRM) *INCT-OBTL-5 Oriental Basma Tobacco Leaves* (Samczyński et al., 2012) according to the same procedures used for studied samples. CRM analyses are reported in Table S1.