Analysis of geochemical tracers in different systems soil-Citrus limon (L.) Osbeck

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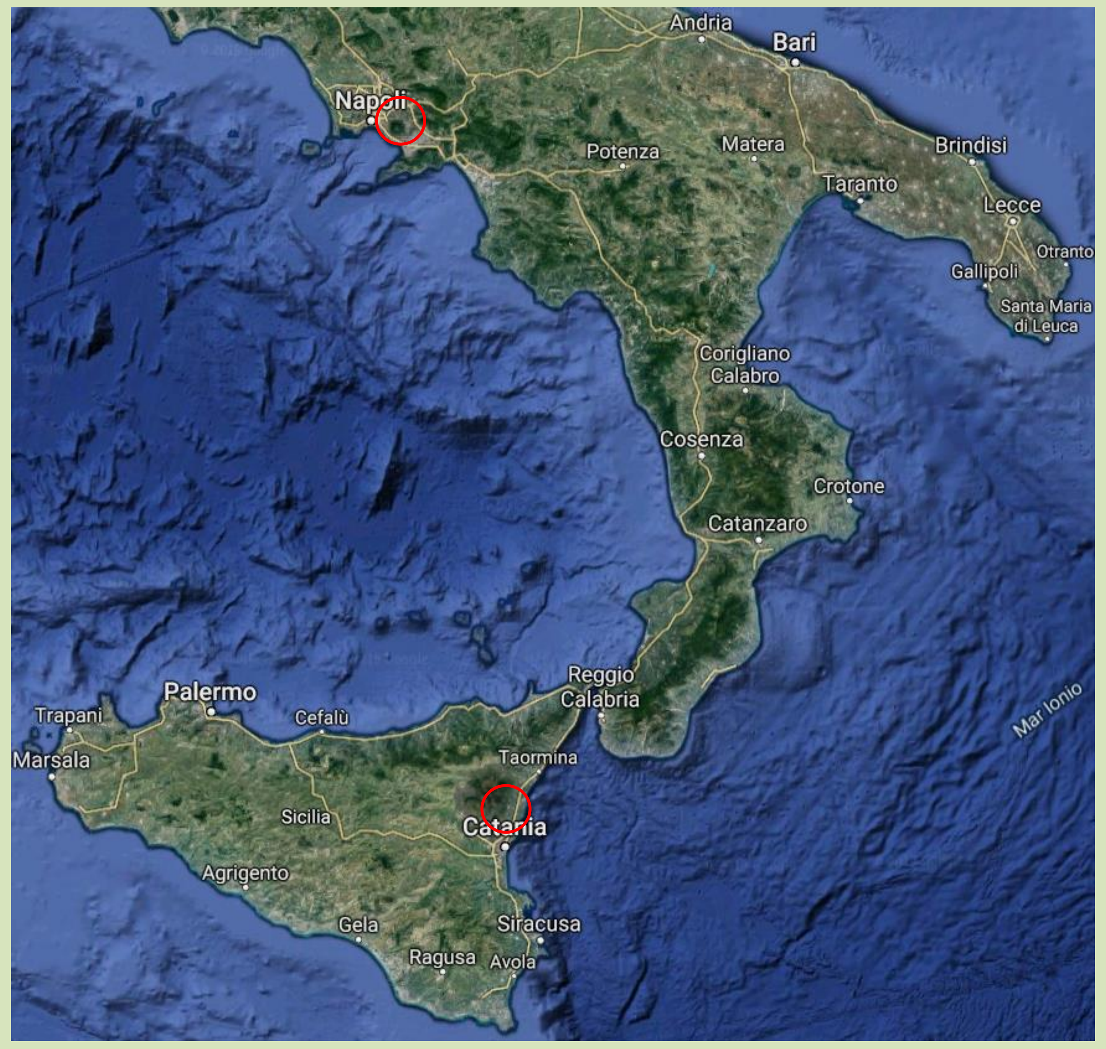
Introduction

Today is increasing the attention of consumers for the origin of food and the high reputation of products with a distinct geographical identity. Food traceability is an important issue in food safety and quality control, with impacts on food security, its quantity, and overall availability. The knowledge of a chemistry relationship between the soil and the agricultural products is an important tool for the quality assessment of food. This study uses rare earth elements (REEs) as geochemical tracers. The REEs are a set of 14 elements, from lanthanum to lutetium that can be divided into light rare earth elements (LREEs), from La to Gd and heavy rare earth elements (HREEs), from Tb to Lu. The REEs have recognized as very useful tracers due to their generally coherent and predictable behavior.

Objectives:

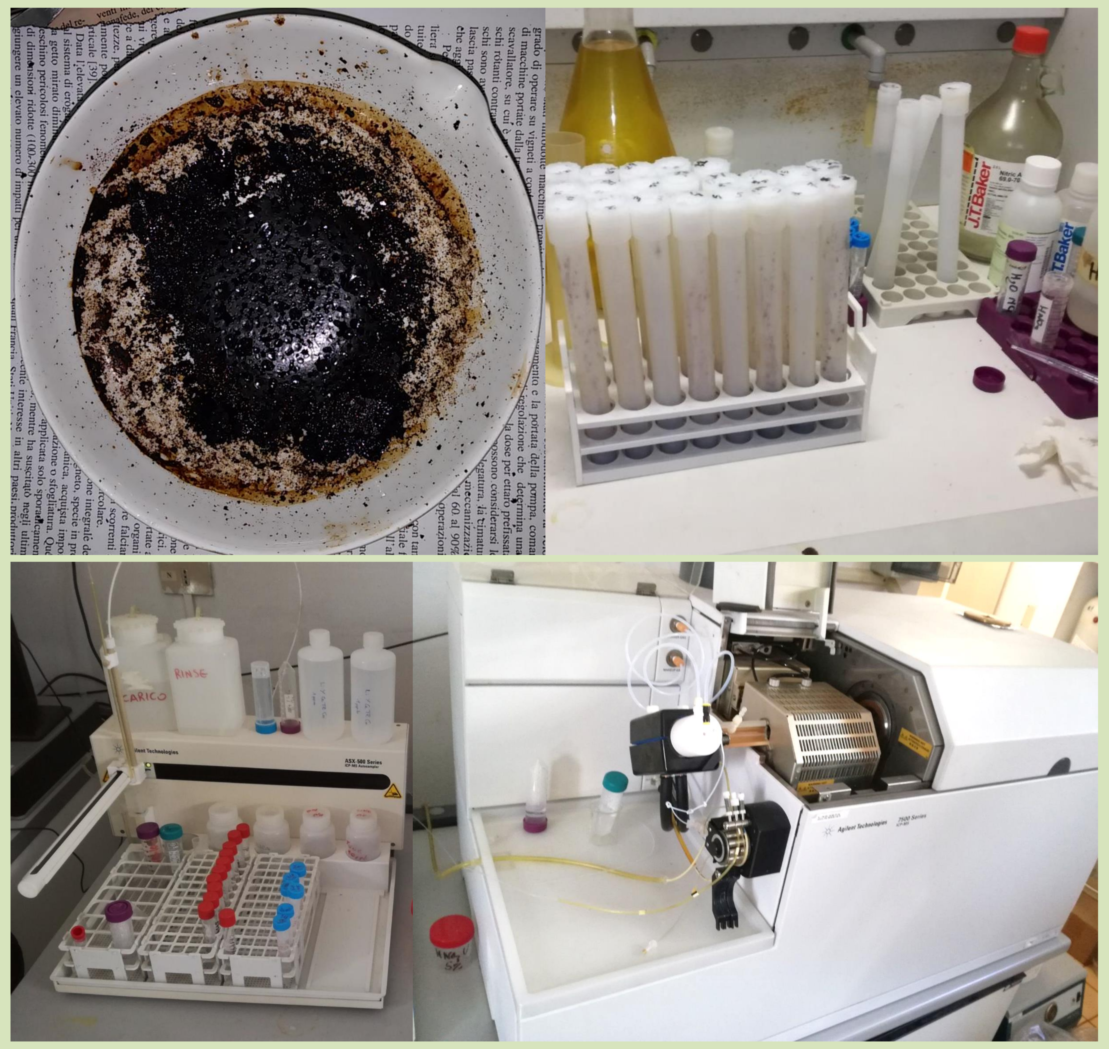
The research aims to observe whether the fruits of various cultivars of citrus cultivated on the same soil and their products (fruit and juice) reproduce the same distribution of REEs.



Materials and methods

Ten different varieties of Lemon fruits (Citrus limon Osbeck (L.)) were sampled: Akragas, Erice, Selinunte, Segesta, Continella, Femminello Siracusano, Femminello Dosaco, Kamarina, Sfusato, Ovale di Sorrento, Interdonato. Lemon plants were grafted onto a unique rootstock (Citrus × aurantium L.), grown on volcanic soil in two experimental farms, located at the "Acireale" (Ct) region (latitude 37°37'23 N, longitude 15° 09'51 E and 205 m a.s.l., in Sicily, Italy) and "Portici" (Na) region (latitude 40°81'55 N, longitude 14°34'75 E and 75 m a.s.l., in Campania, Italy).

A sample of 2 kg of fruit was collected at technological ripeness from each plant of three for every cultivar. As well as, three soil samples (about 2 kg) in the field corresponding to lemon sampling were collected and to reduce any surface contamination from a depth of 10–30 cm. Aliquots of sample (soil, fruit, juice, and peel) dried at 105°C and ground, were mineralized (M) in Teflon containers with HNO_3 and H_2O_2 concentrated in a microwave oven. For the determination of REE's bioavailable part, 20 g of soil were stirred with 100 ml of DTPA solution (0.005 M, pH 5) for 24 hours. Quantitative analysis of REEs (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) was performed with an Agilent ICP-MS 7500ce, operating in quantitative mode with external calibration and internal standard online (^{187}Re 1mgL^{-1}). The REEs amount expressed in nmol kg^{-1} of dry matter , the HREEs/LREEs relations and their distribution in the fruit and citrus juice concerning for to the own soil were determined and calculated.



Results:

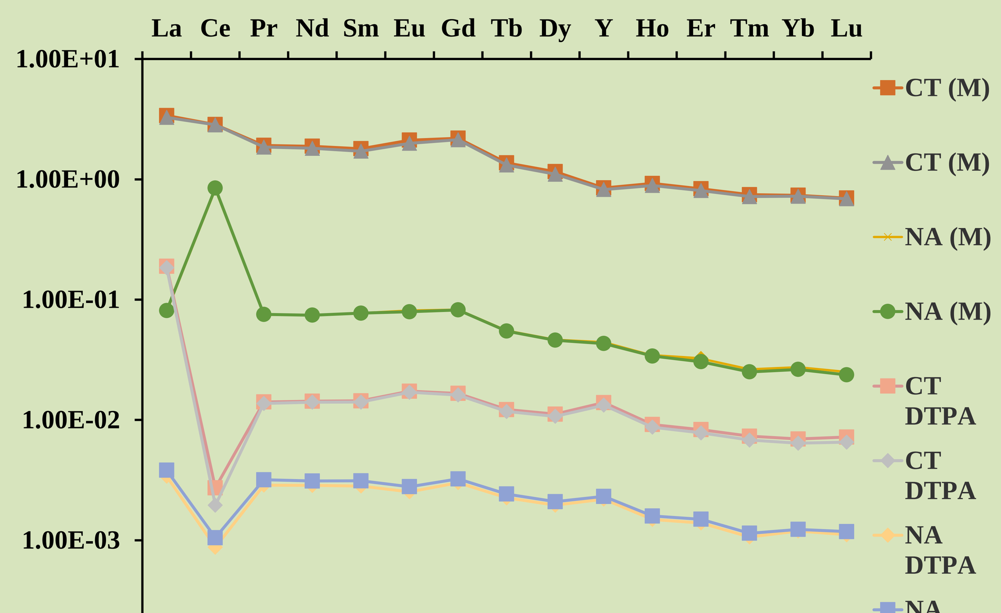


Figure 1 **REEs Soils**

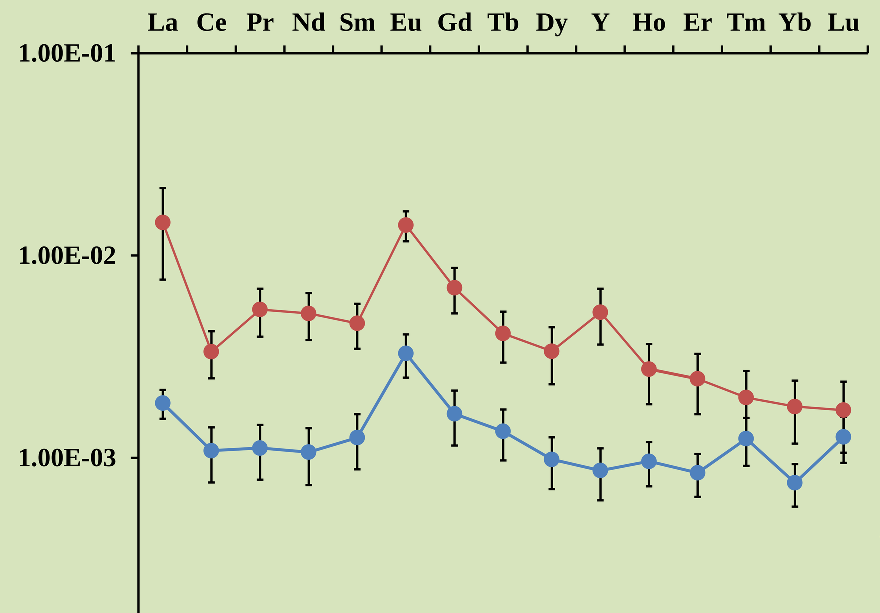


Figure 2 **REEs Fruits UCC pattern**

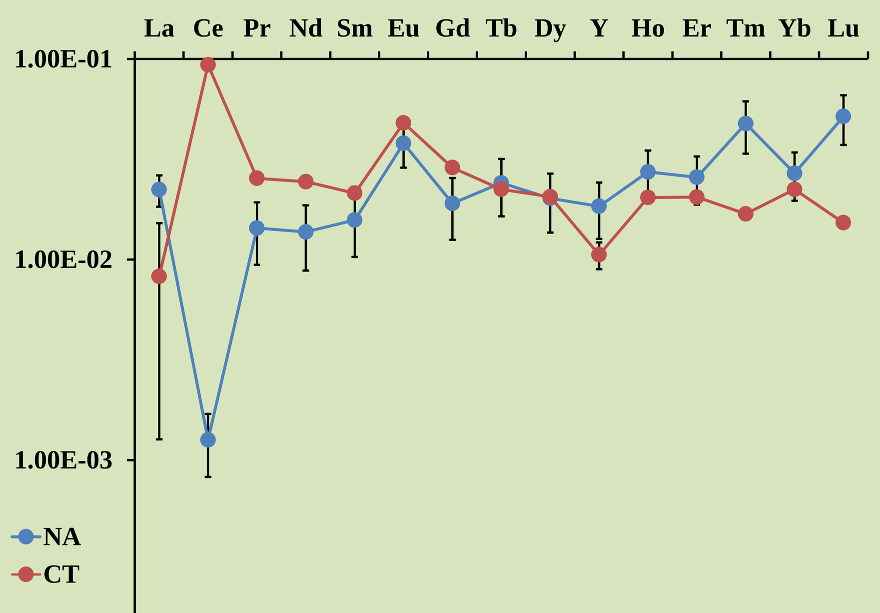


Figure 3 **REEs Fruits Soil (M) pattern**

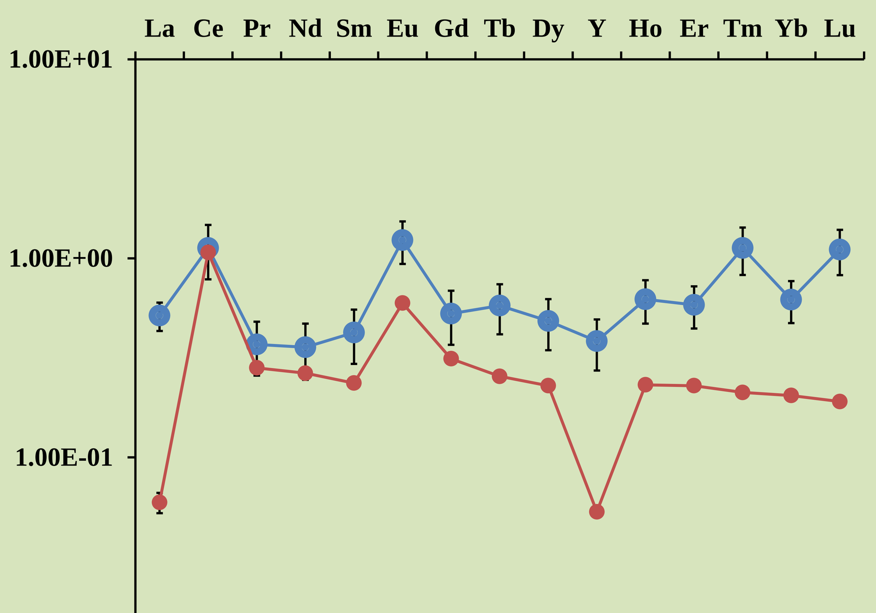


Figure 4 **REEs Fruits Soil DTPA pattern**

The good spatial homogeneity of the studied area is given by the values of the standard deviations found among the soil samples reflecting the hypothesis of the "similar soil" (Figure 1), for the REE elements. The REE pattern for the different cultivars shows strong similarities of all REE distributions confirming the identical behavior of every cultivar in the uptake of REE. The different cultivars were not able to induce significant differences in REE uptake from the soil maintaining the same fingerprint except for Eu (Figure 2, 3, 4). It is also noted that the two different extraction methods (M, DTPA) influence the absolute quantity extracted but not the REE patterns. The difference in quantities results also in the different parts of the fruit: in the skins, the quantity detected is greater than the fruits, but newly the fingerprint is unchanged. Previous works, based on the geochemical behavior of REEs in the Vitis vinifera/soil system [1,2] indicated that there is no fractionation of REEs in the passage from soil to grapes and from grapes to must. It was therefore interesting at this stage to check whether the distribution of REEs in soil forms a fingerprint maintaining in fruits an juices. In this study, the graphs show that the original fingerprint of the soil is well maintained in the fruit but also in the juices. The "anomalous" behavior of europium can be explained with its similarity with Ca^{2+} ion. In the analysis of REEs data it is possible to exploit the potential of the HREEs/LREEs ratio. Regarding fruit and juice samples, we evaluated HREEs/LREEs ratios for different cases (Fig.5-11) and we found always high R^2 values, regardless of any soil-plant-cultivar combination: all plants showed the same correlation pointing out that the cultivar effect is deleted and depends exclusively on the species. Within the standard deviation, the differences between the data are negligible.

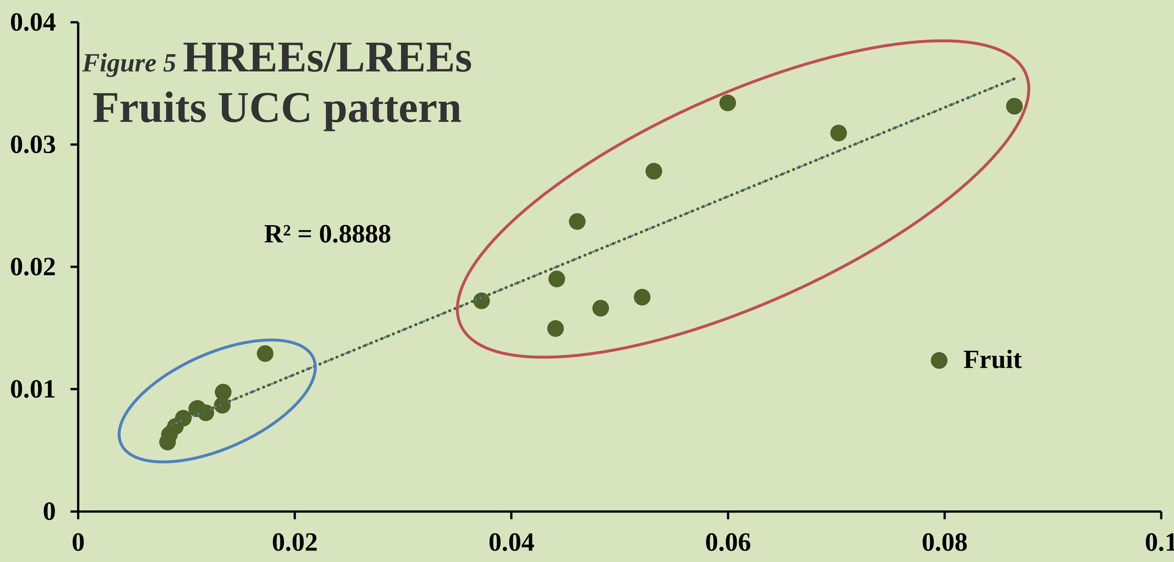


Figure 5 **HREEs/LREEs Fruits UCC pattern**

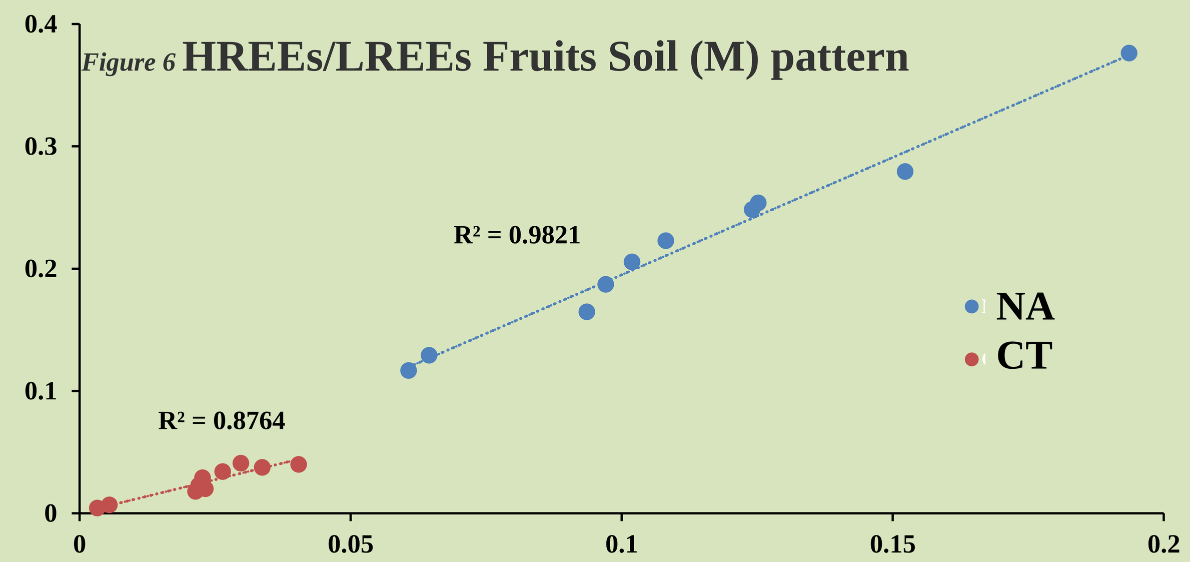


Figure 6 **HREEs/LREEs Fruits Soil (M) pattern**

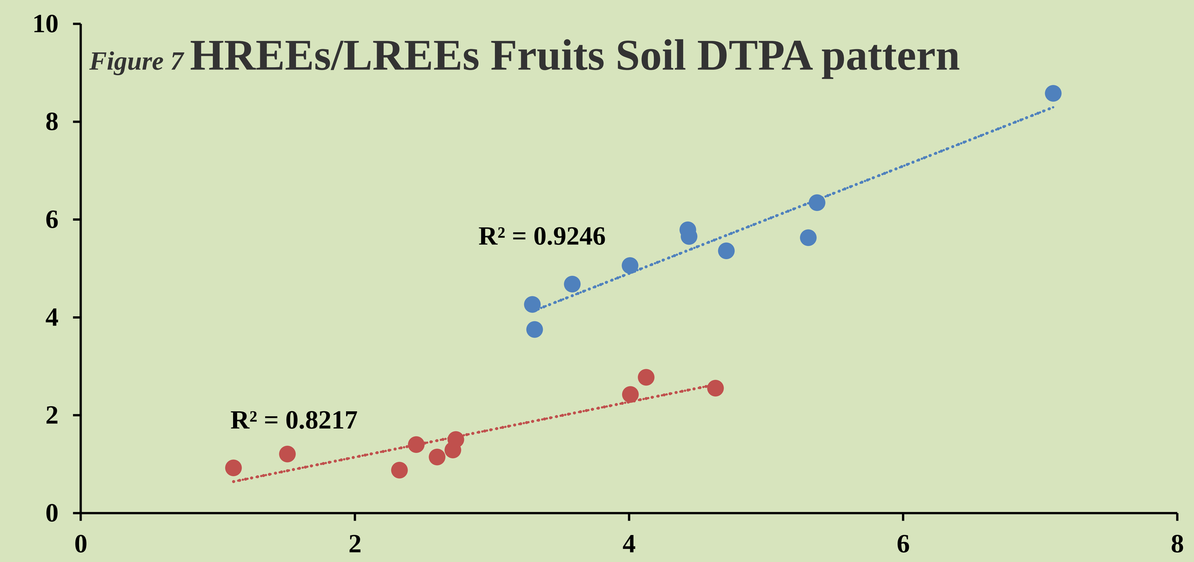


Figure 7 **HREEs/LREEs Fruits Soil DTPA pattern**

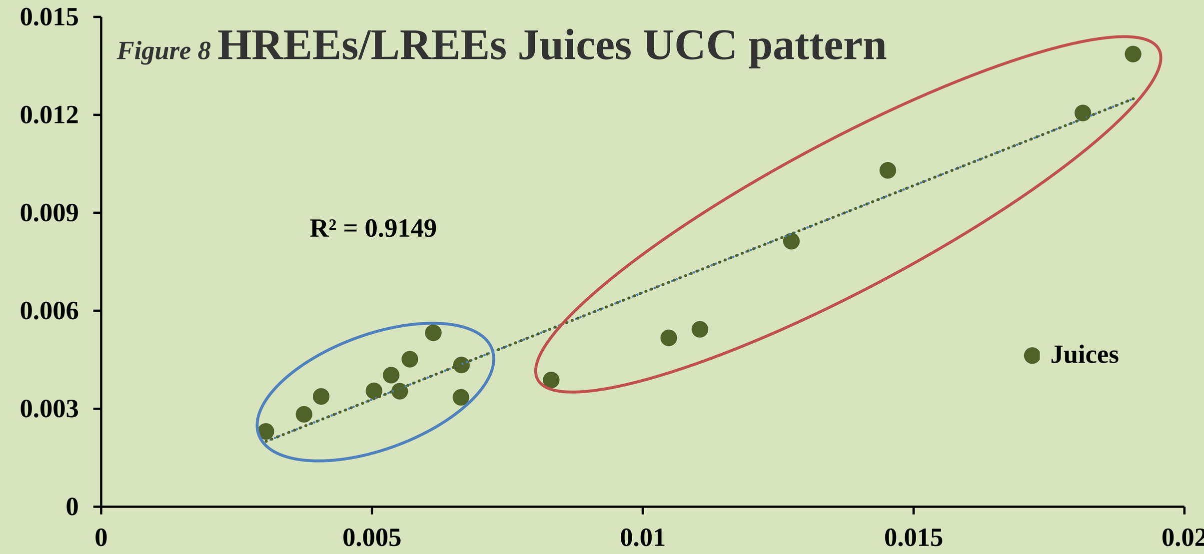


Figure 8 **HREEs/LREEs Juices UCC pattern**

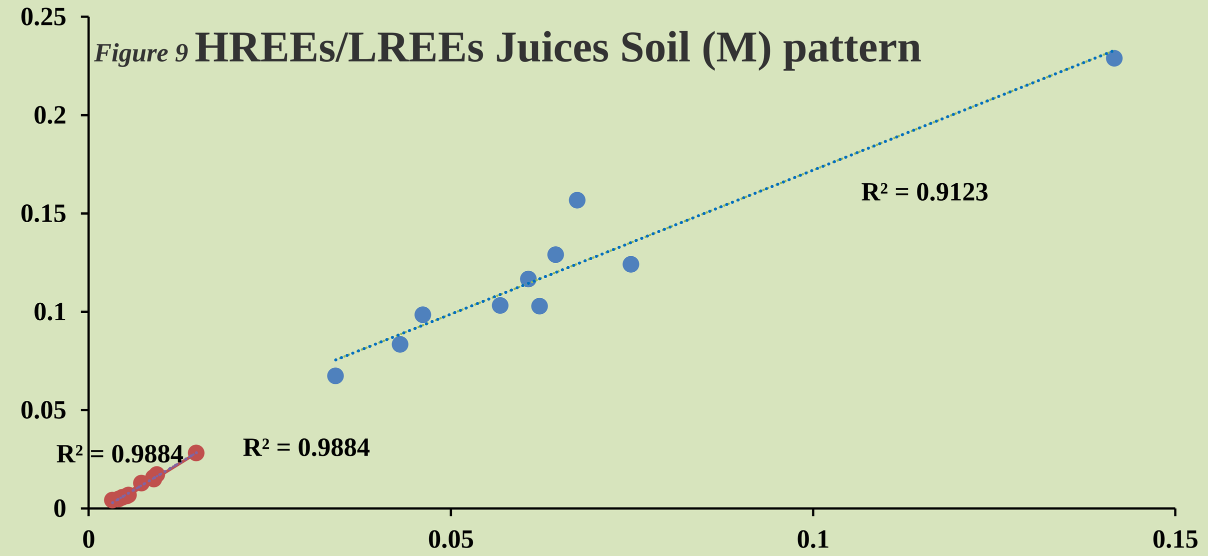


Figure 9 **HREEs/LREEs Juices Soil (M) pattern**

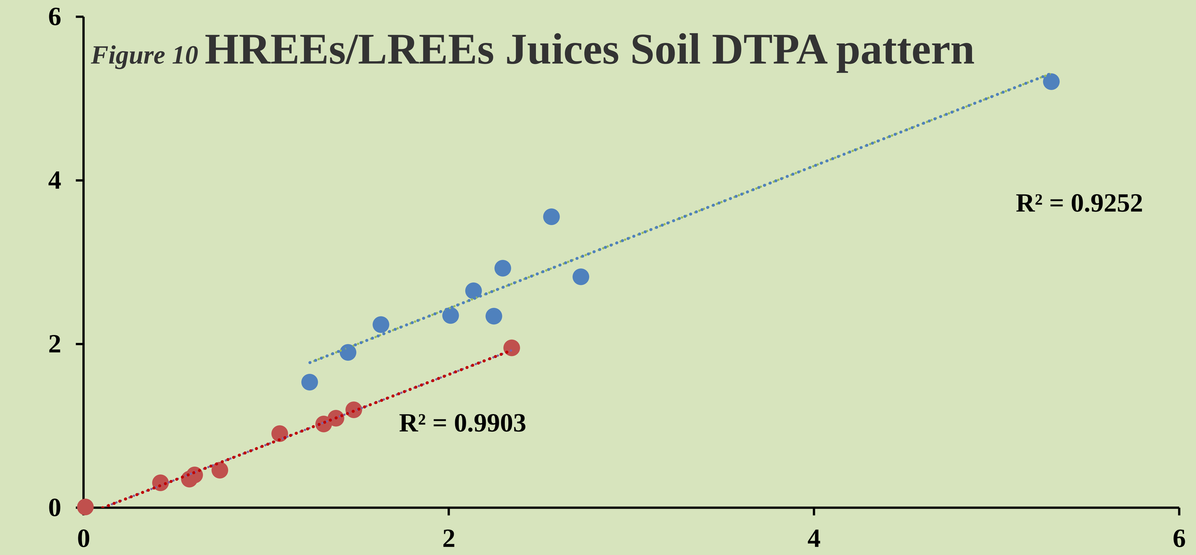


Figure 10 **HREEs/LREEs Juices Soil DTPA pattern**

Conclusions

- **Preliminary results have been obtained on the transfer of REE from the soil to the fruits and lemon juices.**
- **The results obtained show that the REEs schemes of lemons of different cultivations depend only on land distribution.**
- **The REEs approach could be a versatile tool for connecting soil and lemon products, for a geographical characterization.**

References

[1] A.Pisciotta, L.Tutone, F.Saiano Food Chemistry. 2017, 221, 1214–1220

[2] P. Censi, F. Saiano, A. Pisciotta, N. Tuzzolino Sci. Total Environ. 2014, 597–608