The distribution of Rare Earth Elements in *Vitis vinifera L.* discriminates the substrate of growth

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Highlights

Rare Earth Element pattern in *Vitis vinifera L.* plants discriminate natural from contaminated soils
Roots primary accumulate REE from contaminated soils
The mass of *Vitis vinifera L plant* in not affected by REE contaminated soils

Abstract

Sustainable agricultural, food-related strategies and geographic traceability require understanding of the plant physiological response to stress potentially generated by contaminated soils. Here, the effect of contaminated substrate on growth of *Vitis vinifera L*. plants was investigated analysing the distribution of full Rare Earth Elements (REE) spectra in different parts of the plant. Experiments were carried out using pristine plants growing in a handmade substrate (blank experiments) and REE artificially-enriched soil (spiked experiments). We found that both plant mass and REE amount in leaves are not influenced by the substrate enrichment while roots are by one order of magnitude enriched for three orders of magnitude enhancement of the soil substrate, indicating that soil contamination does not significantly influence the REE amount in the plant aerial parts. However, the REE distribution spectra reveal that Light-REE (LREE) and Heavy-REE (HREE) behave differently as a function of the soil conditions: we found that the ∑LREE/∑HREE ratio in the spiked experiment is by one order of magnitude higher compared to blank experiments. We propose that REE distribution discriminates the substrate of growth of *Vitis vinifera L* thus providing a helpful tool for the geographical tracing of agri-food products.

1. Introduction

The identification of foodstuff provenance is of significant importance for quality control, food safety and adulteration pushing consumers and legislators for clear identification of the food geographical origin (Richter et al 2019). The social and economic extent questioned also the European Union that estimates the cost of food fraud by 8–12 billion euro per year (European Commission, 2019) advocating the urgency of food authenticity and product quality (Brunner et al., 2010; Drivelos and Georgiou, 2012; Marchionni et al., 2016). We focused on *Vitis vinifera L.* growth because grapevine cultivated worldwide for fruits, wine and juice (Laucou et al., 2018; Vivier et al., 2002) adapts in different soils and climates (Soneji et al., 2011). We questioned the plant physiological response to Rare Earth Elements (REE) contaminated soil evaluating the transport from soil to plant in view of discriminating polluted soil from the 'natural' one. REE consist of 14 unique elements from ^{58}Ce to ^{71}Lu (Lanthanide series) that associated with Y and La are characterised by the progressive filling of the 4f orbitals. REE have similar chemical and geochemical behaviour in solids while are governed by interface processes in liquid-surface reactions both with inorganic and organic materials (Censi et al., 2015; Vermeire et al., 2016). The REE spectra may also reflect complex reaction mechanisms of soil-plant transfer (Brioschi et al., 2013; Liang et al., 2008; Tyler, 2004) making then potential tracers for food-product quality (Aceto et al., 2013; Bertoldi et al., 2009, 2011; Bettinelli et al., 2005; Censi et al., 2014; Oddone et al., 2009; Pepi et. al 2016, 2017, 2018; Pisciotta et al., 2017; Punturo et al., 2018;).

In plants, the distribution of REE is of potential interest for identifying the geographical origin of agri-food products as these trace-metals are emerging environmental contaminants resulting from increasing technological uses and agricultural practices (Li et al., 2013; Miao et al., 2011 Pagano et al., 2015a). A relation between REE content in plant and human body transfer is not completed established while the toxic effect of REE has been identified in bacteria, animals and humans (Censi et al., 2011; Durães et al., 2014; Feng et al., 2006; Jiang et al., 2012; Krzciuk and Gałuszka, 2019; Pagano et al., 2015b; Turra et al., 2018; Wang et al., 2017).

REE behaviour in plants was generally investigated in dose-response studies during hydroponic growth making critical the extension to real-growth situations (Thomas et al., 2014). For this purpose, we investigated the REE distribution in different parts of the plant during one-year long experiments using two

different substrates: one with a handmade substrate (blank experiments) and another with the same substrate but artificially enriched in REE (spiked experiments). We questioned if during growth an enriched substrate could influence the mass of *Vitis vinifera L.* and metal accumulation in the different plant organs. Evaluating the REE transport from roots to the aboveground organs using the full REE distribution spectra, we want to evaluate if the different soils of growth can be discriminated by the analysis of the final product. Pioneer works on *Vitis vinifera L.* adopted a multivariate statistic approach (Aceto et al., 2013; Bertoldi et al., 2011) while recently the REE properties were proposed as a possible tracer of soil-grape reactions (Censi et al., 2014; Pisciotta et al., 2017). We focused on a controlled experimental approach and report evidence of REE fractionation between native soils and plant organs establishing possible discrimination of the growth environmental conditions of *Vitis vinifera L*.

2. Materials and methods

1.1. Experimental set-up

Thirty pristine *Vitis vinifera L*. individual plants (Moscato d'Asti, rootstock 1103 P) of one year in age from native soils were used in an off-soil experiment at the Department of Agricultural Food and Forest Sciences of the University of Palermo (Italy). The choice of experimental substrate is fundamental because REE mobility depends on complexation reactions with the main substrate components and root exudates. We selected a gravel and peat substrate constituted by humic acids meanly and low REE content (REE values are lower than the quantification limit (LOQ). See Supplementary Material). We assessed the plant physiological response to contaminated soils (spiked experiments) enriching by 3 orders of magnitude the experimental substrate (blank experiment). REE determined in the experimental substrate are lower than 0.9 nmol/kg (maximum value of the quantitation limit). Therefore, the addition of 2.5 µmol per Kg of each REE corresponds to an enrichment of at least 3 orders of magnitude. (REE quantitation limit values are reported in the supplementary materials).

Pristine plants were put into polyurethane pots with 5 Kg of a homemade substrate with a peat-gravel ratio of 2:3 w/w. Before planting, the root length was uniformed to 10 cm to assure an equivalent development.

Two different growth conditions were investigated: one using the homemade substrate (blank experiment) and another adopting the same substrate spiked with 2.5 µmol per Kg of each REE (spiked experiment) (Fig.1).

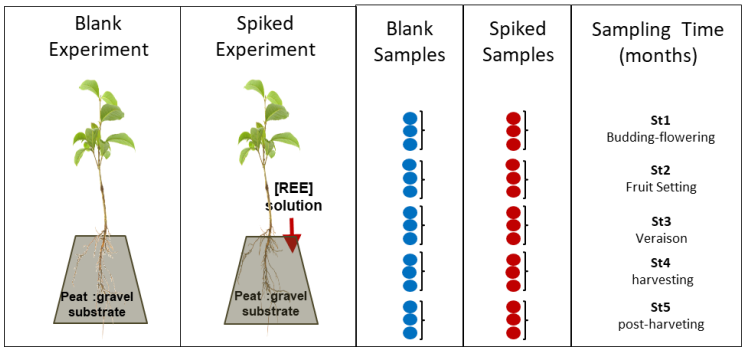

Figure 1. The off-soil experimental system

In both experimental conditions, plants were homogeneously irrigated avoiding material loss by leaching and stress while not disease spray was used. Sampling was carried out at five different growth stages (St) selected according to the different plant-life periods: budding-flowering (2 months), fruit-setting (3 months), veraison (5 months), harvesting (8 months), post-harvesting (10 months). Each sampling was replicated three times and for every sampling time plants were separated in roots and aerial parts. Roots were in turn separated in woody (Ø ≥ 2mm), middle (1mm ≤ Ø ≤ 2mm) and fine-roots (Ø ≤ 1mm), while aerial parts consist in leaves and herbaceous shoot, petioles, wood shoot (one year old), wood shoot (two years old). The REE determination was performed for every sampled part. The experiment was conducted in a green-house, therefore the potential influence of particulate contamination was not considered (Bargagli, 1998). The influence of the atmospheric fallout on leaves was recently observed (Censi et. al., 2017) and contamination was identified in areas with a high anthropogenic impact (oil refineries and power stations).

1.2. Analysis

1.2.1. Sample preparation

Ultrapure grade reagent, nitric acid (65%), hydrogen peroxide (30%) and standard solutions (yttrium, lanthanides and rhenium, each 1000 ± 5mg/L), were purchased from BDH, Merck and CPI International (Italy) while ultrapure water 18.2 MW cm^{-1}, produced with an EASYpureII (Thermo, Italy), was used. Every part of the plant was weighed, chopped, dried (105°C for 24h), grounded in an agate mortar and stored in a PE

vessel. 0.500 g (DW, dried weight) of each sample was transferred in a Teflon vessel with 4.5 ml of 2:1 v/v mixture of HNO_3:H_2O_2 and put in a microwave-assisted oven. After digestion, the extracts were quantitatively transferred into a graduate polypropylene test tubes and diluted with ultrapure water to 10 mL. The substrate samples were dried in an oven at 105°C, gently crushed, sieved (Ø 0.5 mm) and homogenized. Aliquots of 0.250 g (DW) were digested in a microwave system. After digestion, the extracts were quantitatively transferred to a graduated polypropylene test tube and diluted with ultrapure water to 100 mL. Each analytical sequence included a procedural blank (ultrapure water digested as the other samples).

1.2.2. Chemical measurements

REE concentration was measured by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using the Agilent Technologies 7500ce Series Spectrometer using forward power: 1550 W; nebulizer gas flow: 1.00 L/min; auxiliary gas flow: 0.85 L/min and plasma gas flow: 15 L/min. The acquisition time was 180 s and three replicates were realised. Analyses were carried out with an external calibration method in the range between 1.0 and 10.000 pg/mL, for every investigated element (^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb ^{163}Dy, ^{89}Y, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu) while ^{187}Re (1000 pg/mL) was used as the internal standard. The stability test was performed before each analysis monitoring ^{7}Li, ^{59}Co, ^{89}Y, ^{140}Ce, and ^{205}Tl masses and adopting at least 2% of precision. The oxide and doubly charged ion interferences were controlled verifying that CeO^+/Ce^+ and Ce^{2+}/Ce^+ ratios were less than 0.5%. The eventual spectral interferences of polyatomic barium ions on the europium isotopes estimation was evaluated using the certified standard INCT-OBTL-5 Oriental Basma Tobacco Leaves (Samczynski et al., 2012).

1.2.3. Data quality assurance

The quality of the REE analytical determination, linearity, precision, sensitivity and recovery of the method was evaluated. Specifically, linearity (regression coefficient and dynamic range) was evaluated by a duplicate of eight standard solutions. The correlation coefficient was higher than 0.99 for all REE in the 0.001 - 10 µg/L working range. The precision (repeatability), expressed as relative standard deviation percentage (RSD%), was determined by six repetitions of each calibration level while RSD% was less than 5% for all measured

elements. The detection limit (DL) and quantification limit (QL) were determined by six repetitions of calibration blank solution (1% ultra-pure HNO_3) through the following relations:

$$DL = \mu b + 3\,\sigma b \quad (1)$$

$$QL = \mu b + 10\,\sigma b \quad (2)$$

where μb is the blank signal and σb is the deviations standard of the blank. The recovery was estimated by the INCT-OBTL-5 Oriental Basma Tobacco Leaves certified standard material (Samczynski et al., 2012) and values lower than QL were not considered. The recovery percentage ranged between 85% and 111% (data reported in supplementary material) while the error was estimated by the following propagation Eqn3 (Ambrus et al., 2004):

$$\frac{\sigma Q}{Q} = \sqrt{\left(\frac{\sigma a}{a}\right)^2 + \left(\frac{\sigma b}{b}\right)^2 + \cdots + \left(\frac{\sigma x}{x}\right)^2} \quad (3)$$

where σ is the standard deviation associated with the measured value (a,b,x), expressed as relative percentage uncertainty, and Q is the uncertainty of measurement.

1.3. Data processing

The overall plant development was evaluated by the variation of the dried mass during growth. Possible accumulation of REE in organs was estimated by the concentration in roots and the aerial parts. The Translocation Factors (TF), corresponding to the ratio between the REE concentration in aerial parts and roots (Krzciuk and Gałuszka, 2015) was evaluated according to Eq.4:

$$TF = \frac{[REE]_{aerial\ part}}{[REE]_{roots}} \quad (4)$$

Where: $[REE]_{aerial\ part}$ and $[REE]_{roots}$ are the REE concentration (µmol/g) in both aerial part and root respectively. When TF<1, metal accumulate preferentially in roots, when TF>1, metal accumulate preferentially in aerial part, while when TF < 0.1, the plants tend to exclude the metal (Wang et al 2012).

The variation of REE abundance in different parts of the plant was estimated by the ratio between the sum of light REE (ΣLREE) and the sum of heavy REE (ΣHREE) through the following equations:

$$\left[\frac{\sum LREE^*}{\sum HREE^*}\right]_{aerial\ part/UCC} = \frac{\frac{\sum LREE_{aerial\ part}}{\sum HREE_{aerial\ part}}}{\frac{\sum LREE_{UCC}}{\sum HREE_{UCC}}} \quad (5)$$

$$\left[\frac{\sum LREE^*}{\sum HREE^*}\right]_{Roots/UCC} = \frac{\frac{\sum LREE_{Roots}}{\sum HREE_{Roots}}}{\frac{\sum LREE_{UCC}}{\sum HREE_{UCC}}} \quad (6)$$

where ∑LREE is the sum concentration of the elements from La to Gd, and ∑HREE is the sum concentration of the elements from Yb to Lu plus Y. The subscript "UCC" (Upper Continental Crust) corresponds to the average lithospheric reference. "Aerial part" and "roots", correspond to the REE concentration (nmol/kg) in aerial part and roots respectively. For every sample, the distribution pattern of REE was evaluated normalizing the relative abundance of REE in the different plant organs to the lithological reference (UCC) (Laveuf and Cornu, 2009; Pisciotta et al., 2017).

$$[REE^*]_{native\ soil} = \frac{REE_{native\ soil}}{REE_{UCC}} \quad (7)$$

$$[REE^*]_{roots} = \frac{REE_{roots}}{REE_{UCC}} \quad (8)$$

$$[REE^*]_{aerial\ part} = \frac{REE_{aerial\ part}}{REE_{UCC}} \quad (9)$$

The REE distribution pattern allows promptly evaluates an enrichment or depletion of a group or an individual REE relative to the others. These relative differences are called respectively fractionations or ''anomalies", whose intensities are further expressed by ratios (Laveuf and Cornu, 2009). The possible REE anomalies (Censi et al., 2014) has been estimated by the following Eqns. 10 and 11 :

$$\left[\frac{REE}{REE^*}\right]_{shoots/roots} = \frac{\left(\frac{REE_{shoots}}{REE_{roots}}\right)_i^2}{\left[\left(\frac{REE_{shoots}}{REE_{roots}}\right)_{i+1}\left(\frac{REE_{shoots}}{REE_{roots}}\right)_{i-1}\right]} \quad (10)$$

$$\left[\frac{REE}{REE^*}\right]_{shoots/UCC} = \frac{\left(\frac{REE_{shoots}}{REE_{UCC}}\right)_i^2}{\left[\left(\frac{REE_{shoots}}{REE_{UCC}}\right)_{i+1}\left(\frac{REE_{shoots}}{REE_{UCC}}\right)_{i-1}\right]} \quad (11)$$

where the subscript “UCC”, “aerial part”, “roots” correspond to the REE concentration in the reference material, in aerial part and roots respectively. The subscript “i” indicates every REE of the series, whereas “(i − 1)” and “(i + 1)” are its immediate neighbour, before and after within the series (Censi et al., 2014; Laveuf and Cornu, 2009).

2. Results and Discussions

2.1. Overall transport of REE in *Vitis vinifera L.*

We have initially evaluated the plant mass variation along the 10 months of growth. Fig. 2 shows that in the first eight months, plant weight progressively increased by 4 times in both spiked and blank experiments while later decreased for both experimental conditions reflecting the period of rest corresponding to leave fall. During the time of the investigation, we did not find either plant mass changing between spiked and blank experiments or visible disease such as growth accidents.

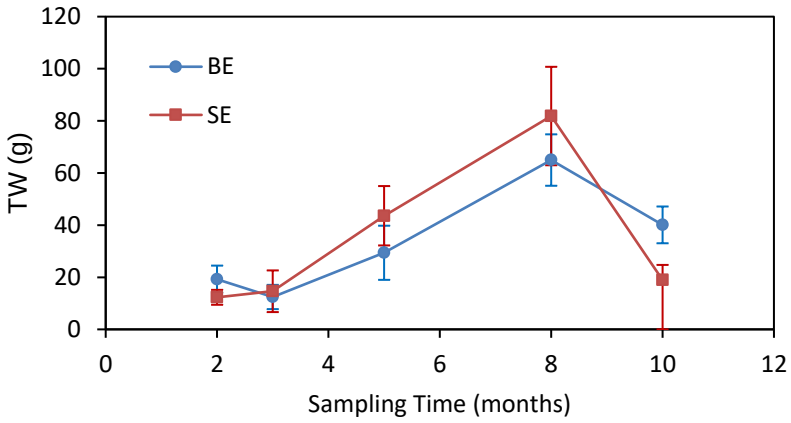

Figure 2. Total Weight (TW) of the plants in Blank and Spiked Experiment (BE and SE respectively) as a function of the time of growth

This indicates that the substrate enrichment does not significantly influence the growth of *Vitis vinifera L.* confirming the behaviour of other plants such as Arabidopsis thaliana, corn (Zea mays) and mungbean Vigna radiate during growth in soils enriched in Ce and La (Diatloff et al., 2008; He and Loh, 2000). However, our results show that in roots the total REE concentration in the spiked experiment is by one order of magnitude

higher compared to the blank suggesting the possible filter role of this parts of the plant (Brioschi et al., 2013).

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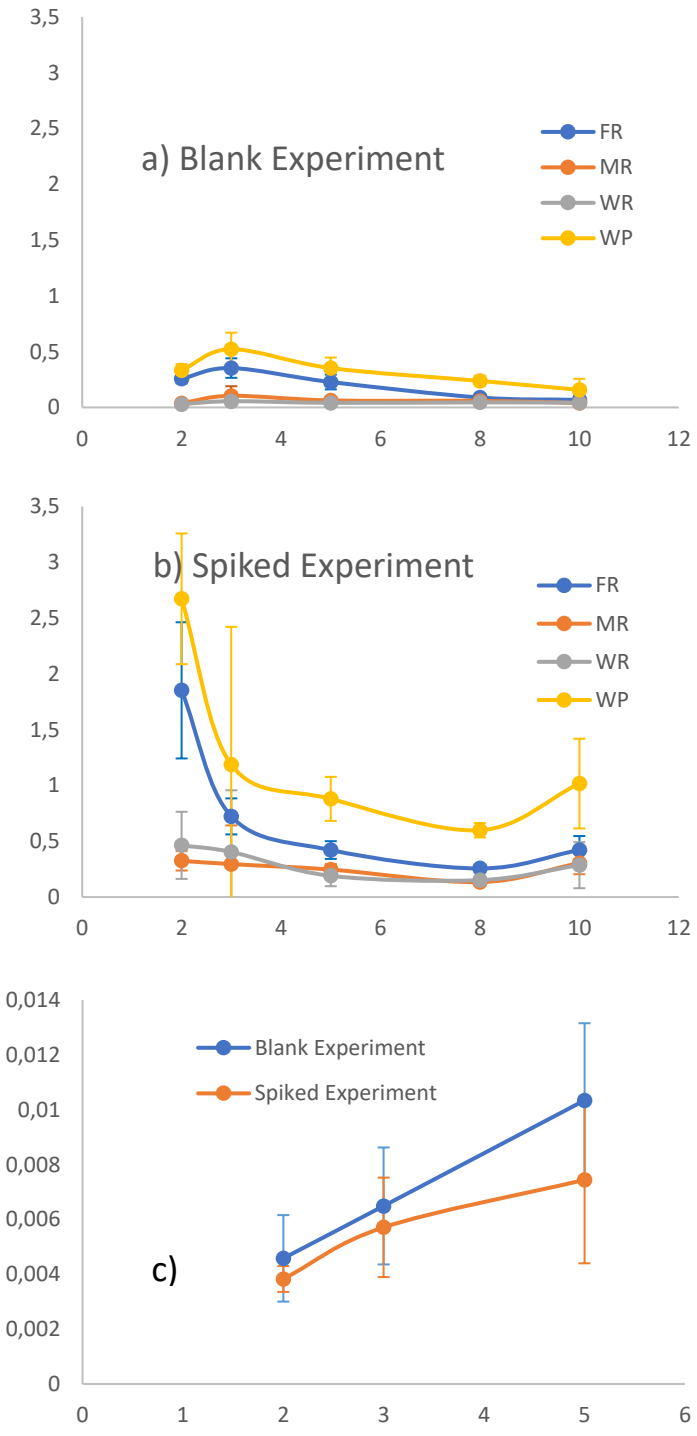

Figure 3.∑REE concentration (µmols/g) in plants organs during plant growth. a) ∑REE concentration Fine Roots (FR), Middle Roots (MR), Woody Roots (WR) and in Whole plants (WP) in the blank experiment. b) ∑REE concentration Fine Roots (FR), Middle Roots (MR), Woody Roots (WR) and in Whole plants (WP) in Spiked experiment. c) ∑REE concentration in leaves in blank and spiked experiments.

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213 Fig. 3 (a and b) shows that the highest REE concentration in whole roots is found in the initial stage (St1) at
214 0.33 ± 0.04 and 2.67 ± 0.88 μmol/g for blank and spiked conditions, respectively, while from S1 to S5 the REE
215 concentration decreases by 2 times in both experimental conditions. The higher value found in the first stage
216 of growth has been found in fine roots more than middle or woody-roots. The preferential enrichment of
217 REE in roots observed in our experiment is in agreement with fine root enrichment in U and Nd found in Scots
218 pine spruce, beech and oak growing from polluted soils (Brioschi et al., 2013; Thiry et al., 2005) and
219 interpreted as corresponding to the greater ability of the fine roots to produce radical exudates compared
220 to medium and large ones (Walker et al., 2003). It is like that through exudation, roots may regulate soil
221 microbial community influencing the chemical and physical soil properties that in turn may affect trace
222 element mobilization from soil to plant (Antoniadis et al., 2017). In leaves, the REE concentration increases
223 linearly during plant's growth spanning from 0.004 (± 0.001) to 0.010 (± 0.002) μmol/g for blank experiments
224 and from 0.0038 (± 0.0004) to 0.007 (0.004) μmol/g for spiked experiments (Fig. 3c).
225 These values are, however, significantly lower compared to that found in roots. Highest amounts were found
226 after eight months of growth (St4), corresponding to the last stage before leaves fall. REE concentrations are
227 on the same order of magnitude in the two investigated conditions despite REE concentration in roots is by
228 one order of magnitude higher in the spiked experiment. Therefore, it appears that *Vitis vinifera L*. limits the
229 transfer of REE maintaining low levels in the aerial parts. REE transfer efficiency in the aerial part of *Vitis*
230 *vinifera L.* has been evaluated for every specific REE at every stage of the growth in the different plants'
231 organs. We found that TF, calculated for both experimental conditions (Fig. 4a, b), is lesser than one for all
232 elements meaning that REE accumulation is greater in roots in comparison with the aerial part.

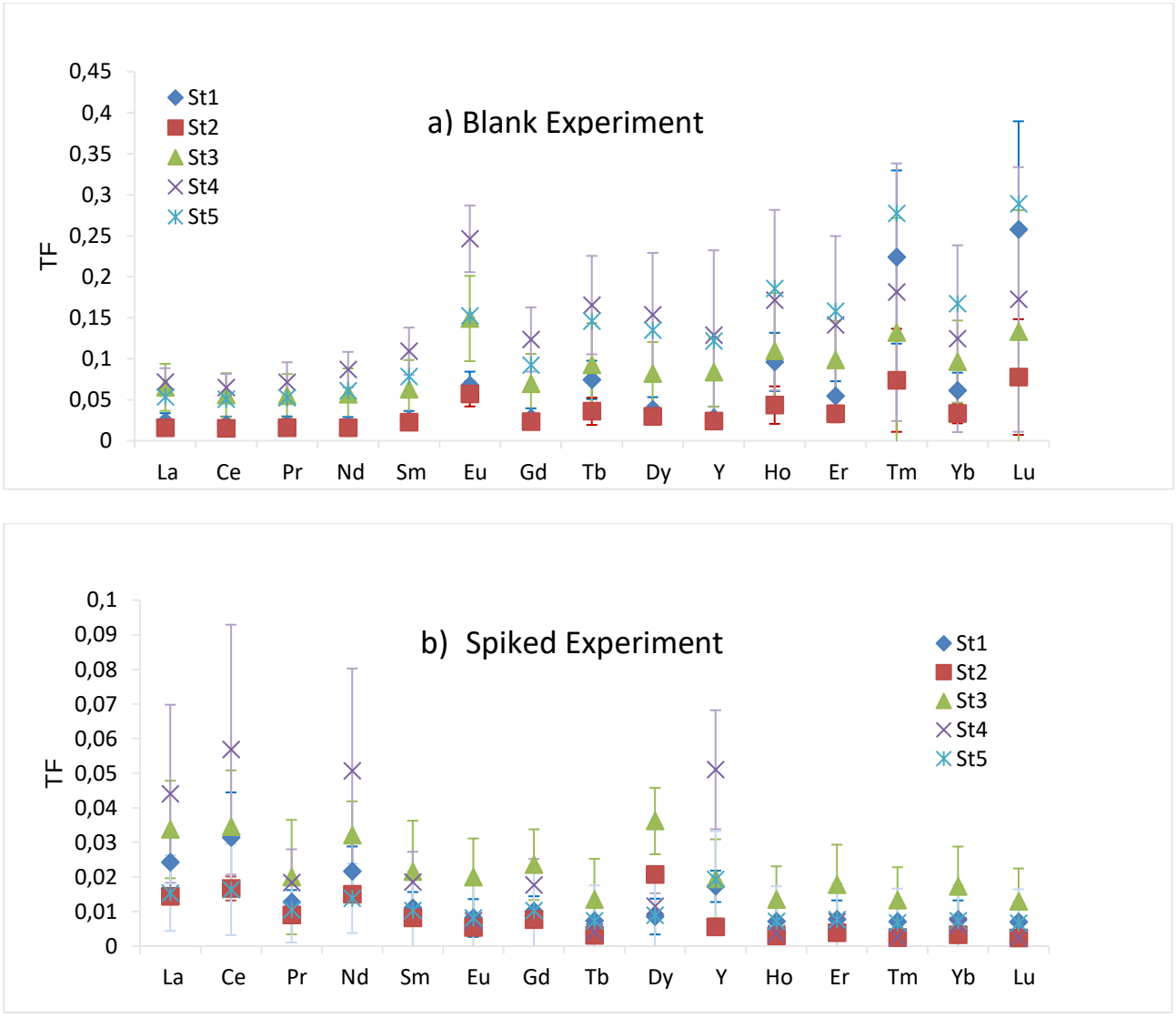

Figure 4. Translocation Factor (TF). a) ratio between REE concentration (µmols/g) in aerial part and roots at each Sampling Time (St1, St2, St3, St4, St5) in the blank experiment. b) ratio between REE concentration in aerial part and roots at each Sampling Time (St1, St2, St3, St4, St5) in the spiked experiment.

Specifically, TF is by 3 to 15 times lower in spiked experiment compared to the blank one. It is important to highlight that in the spiked condition the higher REE amount uptake from roots produces a less transfer capacity to the aerial parts of the plants. This may correspond to a possible detoxification mechanism developed by *Vitis vinifera L* to answer to non-essential, toxic trace element exposures (Pourrut et al., 2011). REE are considered non-essential trace elements entering into plant tissues passively because of their similarity with essential ions (Yuan et al., 2017; Kabata-Pendias and Pendias 2001; Whang et al., 2008). This detoxification process by endodermis cells should correspond to the earlier proposed, *i.e.,* for lead in different species of plants (Pourrut et al., 2011). *Vitis vinifera L.* can transfer even lower amounts of trace

elements as Cu, Zn, Pb or nutrients (N) into berries than in leaves (Araujo et al., 1995; Chopin et al. 2008; Kabata-Pendias and Pendias 2001; Kment et al., 2005). Globally, even if the REE amount transferred is different between the two experimental conditions, the results of our experimental investigation show that the substrate enrichment in REE does not influence the plant physiological response to environmental stress. *Vitis vinifera L*. preferably accumulates REE in fine roots with a likely accumulation strategy governed by processes of exclusion compatible the mass development.

2.2. REE fractionation in *Vitis vinifera L.*

The transfer of REE in the overall plant has been initially estimated by the relative fractionation of REE group using the ratio between Light-REE and Heavy-REE (∑LREE/∑HREE). Fig. 5 shows that the ∑LREE/∑HREE ratio remains constant for every experimental condition and single lines can be parametrised for every condition.

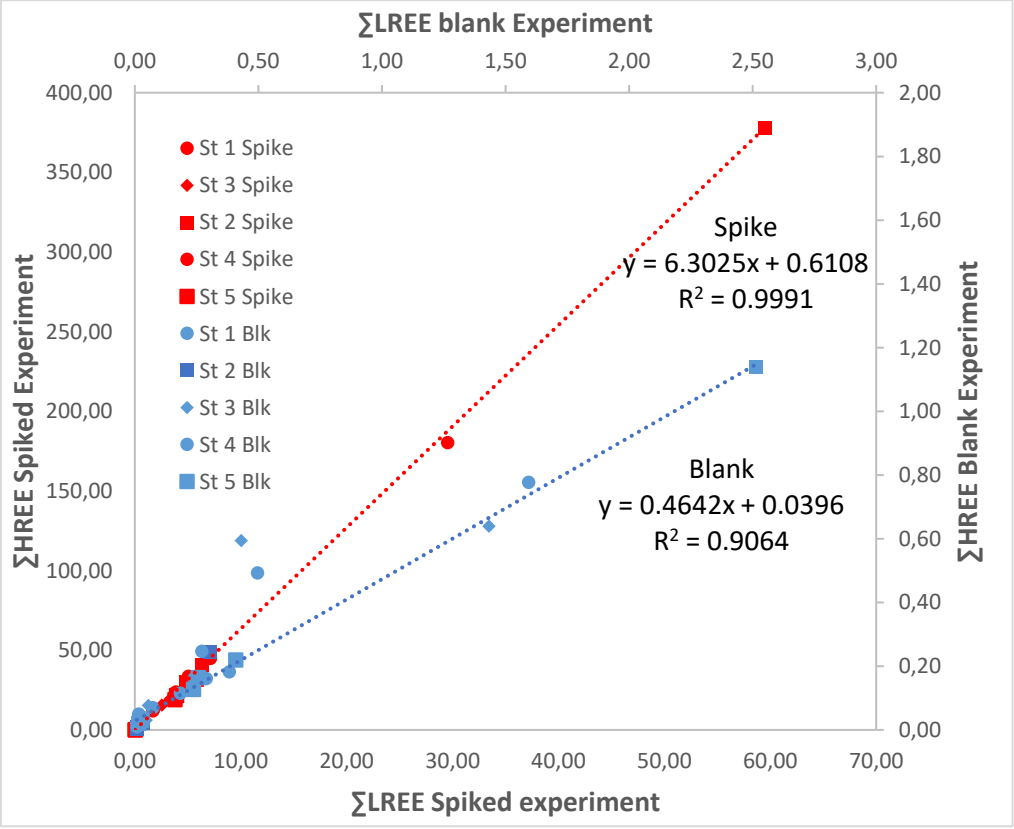

Figure 5. Normalized ∑LREE/∑HREE in plants organs during different growing stages

We found that the ∑LREE/∑HREE ratio in the spiked experiment is by 1 order of magnitude higher compared to the blank indicating the answer of the plant to REE enrichment in the soil. If this enrichment may be

explained by a possible enhancement of complexation reaction between the REE free ions added related to the different apparent REE stability constants (Byrne et al., 1995), the ∑LREE/∑HREE ratio of the entire plant does not appear to give operative information discriminating different growth conditions. We, thus, focused on the content in the different organs.

Figs 6 shows the distribution of REE normalised pattern in roots and aerial part for the two different experimental conditions.

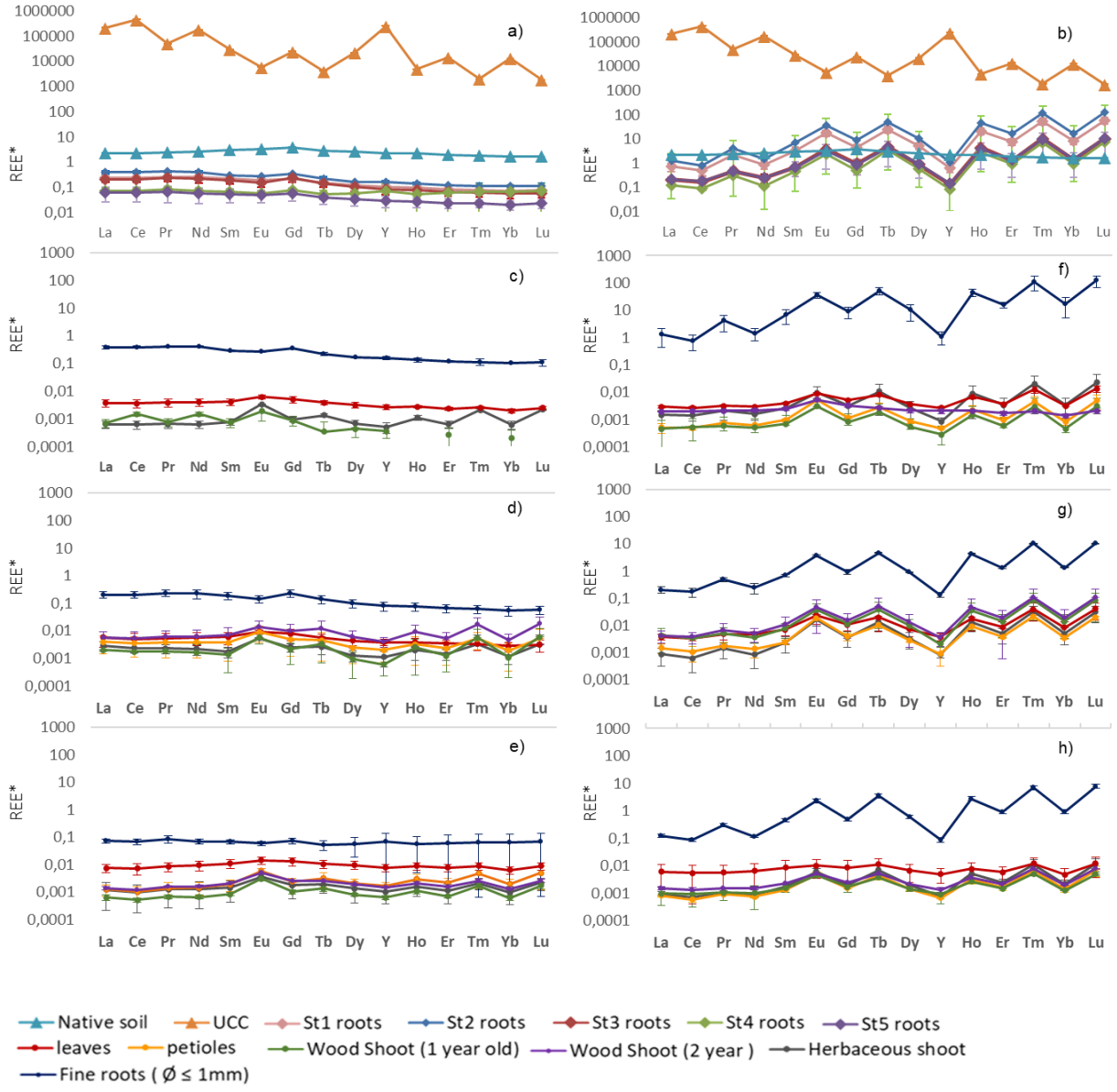

Figure 6. Distribution of REE normalised pattern in plant organ and native soil. a) UCC distribution and REE normalized spectra of native soil and roots for each phenological phases in the blank experiment. b) UCC distribution and REE normalized spectra of native soil and roots for each phenological phases in the blank experiment. c) REE normalized spectra in aerial part and fine roots during fruit-setting (st2) in the blank experiment. d) REE normalized spectra in aerial parts and fine roots during veraison-period (St3) in the blank

experiment. e) REE normalized spectra in aerial parts and fine roots during harvesting-period (st4) in blank experiment. f) REE normalized spectra in aerial parts and fine roots during fruit-setting (st2) in spiked experiment. g) REE normalized spectra in aerial and fine roots during veraison-period (St3) in spiked experiment. h) REE normalized spectra in aerial parts and fine roots during harvesting-period (St4) in spiked experiment

We found that for the blank experiment (Fig. 6a) REE pattern is characterised by a constant decreasing from LREE to HREE reflecting the pristine soil of plant nursery (before being transferred to our experimental pots) as peat-gravel is an inert substrate. Roots, here, have accumulated REE proportionally to the amount of REE of native soil while the higher LREE level compared to HREE may correspond to the enhanced LREE mobility by humic matter in the soil (Coppin, 2002; Ma et al., 2002). Differently, in spike experiment (Fig. 6b), the root REE pattern displays increasing from LREE to HREE with a 'zig-zag' shape. Here, the root pattern does not correspond to native soil and is symmetrical to the UCC distribution in agreement with the equimolar plant absorption of REE. Our results indicate that the REE transport in *Vitis vinifera L.* is not selective depending mainly on the amount of REE that is present in the growth substrate: in the blank experiment, roots reflect the native soil, in spiked experiment mirror UCC. In the blank experiment (Figs 6 c,d,e,), the REE pattern in aerial part displays the general constant decreasing from LREE to HREE in agreement with root pattern with the revealed Eu positive anomaly (Table 1).

Eu anomaly	***St1***	***St2***	***St3***	***St4***	***St5***
$\left[\frac{Eu}{Eu^*}\right]_{roots/UCC}$	0.72	0.74	0.73	0.66	0.79
$\left[\frac{Eu}{Eu^*}\right]_{aerial\ part\ /UCC}$	1.32	1.33	1.46	1.19	1.13
$\left[\frac{Eu}{Eu^*}\right]_{aerial\ part\ /roots}$	6.42	6.23	5.09	4.49	3.21

Table 1. REE anomalies calculated by Eqns. 10 and 11 in the blank experiment, at each sampling time (St1, St2, St3, St4, St5).

The identified positive Eu-anomaly of our laboratory-controlled growth may correspond to that found during natural growth conditions by Pisciotta et al., (2017) and attributed to the possible physiological Eu–Ca substitution during the metabolic reactions (Brioschi et al., 2013). In the spiked experiment (Figs 6 f,g,h), the REE pattern in aerial part still presents the “zig-zag” shape with the typical increasing from LREE to HREE.

Irrespective of the spiked conditions, we found that the REE pattern of the aerial parts reflects the roots spectra remaining unchanged during the plant's growth indicating that *Vitis vinifera L.* does not significantly fractionate REE during complex reaction mechanism of metal uptakes and transfer. We observed that different normalised REE patterns are thus related to substrate variability. We propose that the REE distribution pattern discriminates the soil of growth: in the natural substrate (blank conditions), the distribution of REE reflects the relative abundance of native soils while in the spiked substrate, the REE distribution pattern reflects the UCC distribution.

Implication and conclusion

Despite the weak toxicity of REE, new applications and developing technologies in the agricultural, automotive and telecommunication sectors may increase the environmental levels of various REE, and in turn, the concentrations exposed to plants. These emerging new source of pollution are still associated in several areas of the world to mining conventional pollution and leaching of REE waste minerals. The results of our experimental investigation reveal that in the case of *Vitis vinifera L*. the transfer efficiency of REE from roots to leaves is lower in polluted substrates compared to unpolluted one, although the roots of polluted substrates are by one order of magnitude enriched in REE. We propose that possible REE pollution in soil should not significantly determine the amount of REE transferred to the aerial parts indicating that grapevine products obtained by *Vitis vinifera L.* cultivations should have a very low amount of REE. The results obtained in this experimental simulation do know to show clear evidence of REE possible competition with calcium in calcium-mediated biological processes which could account for some of the plant toxicity.

Evaluating plant physiological response to REE contaminated soil we found that the REE transport in *Vitis vinifera L.* is not selective depending mainly on the level of REE in the substrate of growth. REE distribution pattern keeps unaltered in plant organ: in the unpolluted substrate (blank experiment), roots and aerial part reflect native soil, while in polluted soils (spiked experiment) mirror the UCC. We finally believe that the full REE normalized spectra are a promising helpful tool able to discriminate the substrate of *Vitis vinifera L.* growth meaning that REE may provide an estimation of the geographical origin of this kind of food.

Acknowledgement

This work is part of the doctoral thesis of the first author and supported by Università degli Studi di Palermo and the Sorbonne Université Paris. We wish to thank Dr N. Pisciotta for experimental assistance and Dr L. Oddo for advice.

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Supplementary material

REE Quantification limits

REE	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
LOQ	0,9	0,9	0,9	0,3	0,6	0,2	0,2	0,2	0,1	0,2	0,1	0,2	0,1	0,1	0,2