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# ICP-MS Triple Quadrupole as analytical technique to define trace and ultra-trace fingerprint of extra virgin olive oil

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## Abstract

Extra virgin olive oil is a typical product of Mediterranean area, and its origin protection is continuously improved. 24 olive oil samples from different geographical origin were analyzed and 40 elements were evaluated with chemometric techniques. This study aims at elaborating a method to determine mineral composition of this matrix and at validating the method used to determine its reliability. The high-level laboratory facilities for trace element/isotopic analysis realized in ENEA Brasimone (Italy) is a useful tool to reduce the limit of detection of elements, cutting down pollutants. Both Clean Laboratory for sample pre-treatment and Clean Room Standard ISO 6 are constantly monitored to guarantee the control quality. The results obtained using ICP-MS Triple Quadrupoles show changes between the analysed samples. Finally, Principal Component Analysis was conducted to better characterize olive oil products from different geographical origin, providing a fingerprint of the element patterns in the samples.

**Keywords:** traceability, extra virgin olive oil, ICP-MS-QQQ, rare earth element.

## 1. Introduction

The quality of what we eat has become a real issue highlighting the importance to identify the origin of food commodities for both consumers and producers. European Union Legislation (1992) introduced a discrimination based on Geographical Indicators (European Commission, 2020) testifying the linkage between food and its origin (Council Regulation, 1992). The EU Regulation 178/2002 forced the agro-products traceability requirement.

Unfortunately, it's not always easy to rely on the same parameters for food product's origin determination because of variation due to fertilization, type of cultivation, soil composition and geographical origin. On the opposite, trace, and ultra-trace element (REE) could give a useful representative fingerprint of the composition of the product (Aceto et al., 2018).

To do that, analytical technologies involved in this research are numerous, such as optical spectroscopy and mass spectrometry or atomic absorption spectroscopy. Inductive Coupled Plasma Mass Spectrometry (ICP-MS) is one of the most confident and reliable technique for simultaneous multi-element analysis in traceability. Over the last 20 years, different implementations have been developed, as an additional quadrupole has been introduced in front of the Collision/Reaction Cell (CRC) to act as an ulterior mass filter, obtaining the triple quadrupole (ICP-MS-QQQ) technology. ICP-MS-QQQ leads to a better control over the reaction becoming a powerful tool for the interference-free quantitative analysis especially for rare earth elements. Moreover, with two quadrupoles into the instrumentation, also chemical noise is lower allowing a better sensibility and detectability.

It's largely recognized that edible oil, in particularly from *Olea Europaea* tree, is a characteristic product of the Mediterranean area and a strategic item for its high exportation and consumption. Clearly having a steady growing demand and a high cost of production, Extra Virgin Olive (EVO) oil is much more expensive than other oils and for this reason it may be frequently subjected to adulteration and falsification.

The aim of this study is showing the main mineral composition of EVO oil, which could be apply in a future perspective to illustrate the elements distribution in the matrix. In addition, taking into account different sampling collection areas, the study could be a start to point out significate differences regarding mineral composition, between different origin provenances of EVO oils.

To do this, the use of a triple quadrupole ICP-MS in a Clean Room ISO6 reduces the limit of detection and the limit of quantification of all the elements analysed, and especially the REE elements, which can better discriminate the different kind of EVO oils.

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## 2. Material and methods

### 2.1. Sample collection

The food characterization through mineral fingerprint determination is based on the analysis of EVO oil samples of different origin. The samples were collected in various parts of Italy with some exception sampling in Albany (as shown in Fig. 1), for a total number of 24 olive oil samples (Table 1) from 2013 to 2018 (Rizzo and Telloli, 2019). All the EVO oil samples come from oil mills, except the EVO oil samples from COOP which are industrial, and the specific origin of the olives is not known, it is only known that they are of Italian origin.

**Table 1.** List of the sampling site, specifying the location and the respectively province of the EVO oil samples collected and analysed and the year of production.

Sample name	Location	Province
Albany 2014	Albany	-
Albany 2015	Albany	-
Tuscany 2013	Pistoia	Pistoia (PT)
Tuscany 2014	Prato	Prato (PO)
Marche 2015	Colli del Tronto	Ascoli Piceno (AP)
Liguria 2018	Riviera dei Fiori	Imperia (IM)
Abruzzo 2017	Vasto	Chieti (CH)
Calabria 2015a	Crotone	Crotone (CR)
Calabria 2015b	Castrovillari	Cosenza (CS)
Calabria 2015c	Rossano	Cosenza (CS)
Campania 2015	Perdifumo	Salerno (SA)
Campania 2015	Pimonte	Napoli (NA)
Campania 2017	Perdifumo	Salerno (SA)
Sardinia 2016	Ales (OR)	Oristano (OR)
Apulia 2013a	Barletta	Barletta-Andria-Trani (BAT)
Apulia 2013b	Manfredonia	Foggia (FG)
Apulia 2013c	Molfetta	Bari (BA)
Apulia 2014	Molfetta	Bari (BA)
Apulia 2016	Molfetta	Bari (BA)
Apulia 2018a	Manfredonia	Foggia (FG)
Apulia 2018b	Squinzano	Lecce (LE)
Coop FIORE 2013	-	-
Coop FIORE 2014	-	-
Coop Costanza	-	-

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### 2.2. Chemicals

Sample treatment procedures were optimized by reducing all reagent volumes to prevent sample loss and reducing sample manipulation and possible contamination from consumables or atmosphere. For the blank carrier solution and the digestion acid mixture preparation, 69% solution of HNO<sub>3</sub>, 37% solution of HCl and ultra-pure grade 30-32% H<sub>2</sub>O<sub>2</sub> were acquired from Sigma-Aldrich (St. Louis, MO, USA) and Carlo Erba Reagents (Milan, Italy) respectively. Generally, HNO<sub>3</sub> is used because it favors the oxidation of the almost compounds and minimizes the polyatomic interferences (e.g., Cr, Ni, and As). The high purity deionized water was obtained through Milli-Q® Advantage A10 water purification system (Millipore, Bedford, MA, USA). A multi-element standard stock solution used was the IV-ICP-MS71A (10 µg mL<sup>-1</sup> each in 3% HNO<sub>3</sub>) including 43 elements (Ag, Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ho, K,

78 La, Lu, Mg, Mn, Na, Nd, Ni, P, Pb, Pr, Rb, S, Se, Sm, Sr, Th, Tl, Tm, U, V, Yb and Zn). For the REEs ultra-trace analysis,  
79 the CMS-1 stock Standard solution was selected ( $10 \mu\text{g mL}^{-1}$  each in 5%  $\text{HNO}_3$ ) including 18 elements (Ce, Dy, Er, Eu,  
80 Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, U, Y and Yb). Both standard solutions are produced from Inorganic Ventures  
81 (Christiansburg, USA).

### 82 83 *2.3. Laboratory facilities*

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85 The implementation of high-level laboratory facilities for trace element/isotopic analysis was realized in ENEA C.R.  
86 Brasimone (Emilia Romagna region, Italy), where are present both a Clean Laboratory for sample pre-treatment and  
87 preparation for ICP-MS analysis and a Clean Room (ISO 14644-1 Clean Room Standard ISO 6 class) with controlled  
88 pressure, temperature, and humidity. This clean room satisfies all standard request for food trace analysis, with a  
89 maximum concentration limit (particles/ $\text{m}^3$ ) of  $1 \times 10^6$  for particles equal to and larger than  $0.1 \mu\text{m}$  for ISO Class 6.

90 A Triple quadrupole inductively coupled plasma mass spectrometer (ICP-MS-QQQ) 8800 model (Agilent  
91 Technologies, Santa Clara, CA, USA) is located in the clean room. The instrument configuration includes Nickel interface  
92 cones, standard ion lens and sample introduction system consisting of a MicroMist glass concentric nebulizer ( $400 \mu\text{L}$   
93  $\text{min}^{-1}$ ), a quartz Scott double-pass spray chamber cooled by a Peltier thermoelectric module down to  $2^\circ \text{C}$  to reduce water  
94 vapour present in the sample aerosol, and a quartz shielded torch with 2.5 mm injector.

95 Both the Clean Laboratory and the Clean Room Standard ISO 6 are constantly monitored to guarantee the control  
96 quality which reduce the limit of detection of all the elements, cutting down pollutants.

### 97 98 *2.4. Sample treatment*

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100 The mineralization was carried out with a microwave digestion system, Speedwave Four (Berghof, Germany),  
101 equipped with temperature and pressure parameters control. Each EVO oil samples were weighted 400 mg and directly  
102 put into TFM<sup>TM</sup>-PTFE<sup>5</sup> vessels, a perfluorated plastic with perfluoroalkoxy side chain (< 1% by weight). The vessels  
103 were then filled with 7 ml of  $\text{HNO}_3$  (69%) (Fluka, traceSELECT<sup>®</sup>) and 1 ml of  $\text{H}_2\text{O}_2$  (30%) (Carlo Erba) as acid mixture  
104 for sample digestion preparation. Each digestion cycle was prepared with four closed vessels, and it was programmed  
105 according to the microwave heating program: step 1 with a temperature of  $160^\circ \text{C}$ , pressure 40 Bar for 15 min; step 2  
106 with a temperature of  $100^\circ \text{C}$ , pressure 40 Bar for 20 min and finally step 3 with a temperature of  $50^\circ \text{C}$ , pressure 40 Bar  
107 for 10 min. The mineralization acid mixture already reported was tested with different acid solution ratios and the one  
108 used was with the lowest amount of acid mixture needful for a clear mineralization. Each sample resulting from the acid  
109 digestion was then diluted to 50 ml with the same process solution plus adding 2% of a  $\text{HNO}_3$  69% solution and 1% of  
110  $\text{HCl}$  37% solution. For the multi-element analysis, EVO oil samples were diluted another time with dilution 1:2 with a  
111 final volume of 10 ml. The acid concentration in the final sample was 7.84%  $\text{HNO}_3$  and 0.42%  $\text{HCl}$ . For ultra-trace  
112 analysis EVO oil samples, were analysed as they were.

### 113 114 *2.5. Validation method parameters*

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116 Limit of detection (LOD) and limit of quantification (LOQ) for each element were established for the instrument and  
117 the process, according to EURACHEM recommendation. The first ones were calculated starting from the analysis of five  
118 instrument blanks with three replicate each. Instrument blank means instrument carrying solution: 2% of  $\text{HNO}_3$  and 1%  
119 of  $\text{HCl}$ . To determine its LOD and LOQ standard deviations obtained for each element were multiplied for 3 ( $3\sigma$ ) and for  
120 10 ( $10\sigma$ ) respectively. The same consideration was done for LOD and LOQ calculation for the process, analysing five  
121 process blanks, with three replicate each. The blank of the process refers to the same quantity, 7 mL plus 1 mL of 69 %  
122 solution of  $\text{HNO}_3$  and 30-32 % solution of  $\text{H}_2\text{O}_2$  respectively, analysed with ICP-MS-QQQ after a cycle of acid digestion  
123 and for each sample mineralized.

124 Linearity of the external calibration. Two curves of calibration were obtained. One with eight concentrations point  
125 in the ppb range: 0.1 ppb, 0.5 ppb, 1 ppb, 5 ppb, 10 ppb, 50 ppb, 100 ppb and 150 ppb, for Be, B, Na, Mg, Al, P, K, Ca,  
126 V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, Cs, Ba, Tl, Pb, Th and U. The other for REE in ppt range: 0.1  
127 ppt, 0,25 ppt, 0.5 ppt, 1 ppt, 5 ppt, 10 ppt, 25 ppt and 50 ppt, for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and  
128 Lu.

129 Accuracy. According to the purpose of method's validation, a Standard Reference Material (SRM) was used to testify  
130 the efficiency of the instrument and to determine systematically a possible bias of the analysis. For EVO oil samples it  
131 was not possible having at disposal certified materials with the same or similar matrices, therefore we chose a material

132 with a prevailing organic matrix: SRM-1573A (Tomato leaves) from NIST. It was weighted 0.0200 g of the Standard  
133 Material to be introduced into the vessel for the mineralization. Spiked standard additions consisted in 2 mL of original  
134 Standard solution each time, to obtain in the final sample 16 ppb each element for what concerns multi-element trace  
135 analysis and 40 ppt for ultra-trace REE analysis. The SRM-1573A sample was digested and prepared as explained in  
136 Section 2.3 and analysed with the same approach of the samples. The efficiency of the instrument was verified with the  
137 recovery of the analysed material with known concentrations. To cover the elements, absent in the mineral composition  
138 of the SRM-1573A spiked standards used for the calibration curves were added to the vessel prior to the digestion cycle  
139 to have a complete recovery for each element.

140 Repeatability and inter-day repeatability. Regarding repeatability, SRM-1573A with spiked standard addition was  
141 mineralized and processed by ICP-MS-QQQ five times, with three replicates for each analysis. For inter-day repeatability,  
142 three different mineralization of SRM-1573A with spiked standard addition were digested and analysed within three days,  
143 keeping three replicates for each analysis.

## 144 2.6. *Multivariate analysis*

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147 Multivariate analysis through chemometric methods enables the retainment of the useful information minimizing time  
148 and costs due to the multiple variables related to the observation of a system. Furthermore, chemometric tools application  
149 is required to evaluate the huge number of data resulting from ICP-MS-QQQ analysis, allowing to investigate a possible  
150 relationship between the EVO oil samples and their origin of provenance. Principal Component Analysis (PCA) is one of  
151 the most important techniques to explore and select data information and has found relevant applications in different  
152 sectors, including chemistry, biology, medicine, and economics. PCA works transforming the *original variables* in new  
153 variables called *latent variables*, or principal components, obtained from the linear combination of the original variables  
154 in order to be orthogonal between each other, representing the orthonormal space's basis. First principal component will  
155 represent the maximum variance of the system studied, while the second one, uncorrelated with the first, will represent  
156 the maximum residual variance, and so on until covering the total variance of the system. PCA's relevance is mostly due  
157 to its capacity to reduce the data dimensionality. In addition, this method eliminates the spurious information, it evaluates  
158 each variable's relative relevance, and it allows the visualization of the objects in clusters or in classes, identifying at the  
159 same time the presence of outliers. In this study PCA was performed with XLSTAT by Addinsoft program.

## 160 3. Results and Discussion

### 161 3.1. *Validation method parameters for the multi element analysis*

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165 Two different operation modes were used: *no gas* and He mode. The second one was used to overcome spectral  
166 overlappings due to polyatomic interferences. Interference removal with He in collision mode does not rely on specific  
167 reaction pathways, but through the Kinetic Energy Discrimination a decelerating potential is applied excluding low energy  
168 ions (polyatomic ions and residual gas ions, the ones that have undergone more collisions with He cell gas).

169 Isotopes analysed with *no gas* mode were Be, B, Na, Al, P, K, V, Cr, Mn, Fe, Co, Cu, Se, Ag, Cs, Tl, Pb, Th and U.

170 Isotopes analysed with *He mode* were Mg, Ca, Ni, Zn, Ga, As, Rb, Sr, Cd and Ba. *He mode* was the ones respect to  
171 the other gas available (hydrogen and oxygen) that provided best results according to a high determination coefficient in  
172 the related calibration curve. The optimized parameters were: 3 replicates, 90 sweeps/replicate, 3 points for peak pattern  
173 and integration time between 0.30 and 3 s.

174 LOD for the instrument carrier solution are listed in table S1 (supplementary materials) and expressed in parts per  
175 billion (ppb). LOD parameter has the lowest value for Ag and U with 0.001 ng mL<sup>-1</sup> and the highest ones for Al and P  
176 with 2.170 ng mL<sup>-1</sup> and 1.520 ng mL<sup>-1</sup> respectively.

177 LOD of the process has the lowest value again for Ag, U with also Tl with 0.002 ng mL<sup>-1</sup> while the highest value is  
178 1.440 ng mL<sup>-1</sup> for P and 1.370 ng mL<sup>-1</sup> for K.

179 Linearity. External calibration curve was created on 8 points in parts per billion (ppb): 0.1 ppb, 0.5 ppb, 1 ppb, 5 ppb,  
180 10 ppb, 50 ppb, 100 ppb, and 150 ppb. The linearity of the curve was estimated through the  $R^2$  correlation coefficient for  
181 each element of the multi-standard solution as reported in table S1, together with the isotope of the element, the gas mode  
182 analysis, in a range of calibration between 0.1 and 150 ng mL<sup>-1</sup>. The calibration curve results are strongly linear for each  
183 element, with the highest  $R^2$  number for Be, Rb, Cd, Th and U with a determination coefficient of 1.000 and the lowest  
184 obtained for Ca and Fe with a determination coefficient of 0.9995.

185 Accuracy. The SRM-1573A was used for the determination of B, Na, Mg, Al, P, K, Ca, Mn, Fe, Co, Rb, Sr, Cd and  
186 Ba. Considering that not all the elements included in multi-element standard solution were present in the SRM-1573A,  
187 spiked multi-element standard addition of 2 ml was made to grant an efficient recovery, thus enabling a robust accuracy  
188 analysis also for Be, V, Cr, Ni, Cu, Zn, Ga, As, Se, Ag, Cs, Tl, Pb, Th and U. The volume addition of spiked standards  
189 with SRM-1573A was calculated to yield 16 ppb of each element's concentration in the final sample solution. In table S1  
190 recovery results are reported with relative standard deviation (RSD) as percentage. The element listed with \* represent  
191 the ones determined with the spiked standard additions. Both the SRM-1573A sample and the SRM-1573A with spiked  
192 standards addition were analysed with two different dilutions, 25 times (1:25) to better characterized the minor  
193 concentrations and 100 times (1:100) to better characterized the highest concentration under the prefixed concentration  
194 range. Recovery's value is high for Mg, K, Mn, Fe, Rb, Sr, with full recoveries of the elements. On the opposite, the  
195 lowest recovery value is the one of Ag with a recovery of 61.7%.

196 Repeatability parameter was validated with the reproduction of SRM-1573A sample coupled with multi-element IV-  
197 ICPMS-71A spiked standard addition. The analysis was reproduced five times within one day with three replicates for  
198 sample. Table S1 shows the mean concentration obtained for each element included into the multi-element standard  
199 solution expressed in ng mL<sup>-1</sup> and the RSD in percentage. Each repetition was introduced into the instrument with two  
200 different dilutions, 25 times (1:25) and 100 times (1:100).

201 Inter-day repeatability parameter was validated with the reproduction of SRM-1573A with spiked standard addition  
202 within three days. Three different sample were reproduced from the accurate weigh of SRM-1573A through acid  
203 digestion. Each analysis was developed with two different sample dilution, 25 times (1:25) and 100 times (1:100). As  
204 reported in table S1 almost all the elements were analysed reproducing similar results during different days, thus assure  
205 results validity.

### 206 3.2. Validation method parameters for REE analysis

209 ICP-MS generally has detection limits that are the most conventional for REE covering mass range from 139 uma of  
210 La to 175 uma of Lu. Polyatomic ions often occur as interferences. Therefore, oxide ions from REEs are mostly potential  
211 spectral interferences for middle to heavy analysis. To overcome this overlapping, O<sub>2</sub> reactive gas is used giving higher  
212 detectability and selectivity in respect of the other reactive gases. The optimized parameters for REE analysis were the  
213 same used for multi-element trace analysis. Isotopes analysed with *no-gas* mode were Eu, Tb and Yb. Isotopes analysed  
214 with *O<sub>2</sub> mode* were La, Ce, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm and Lu. Not all the elements are analysed in *O<sub>2</sub> mode*, due  
215 to the non-reactivity with O<sub>2</sub>.

216 LOD and LOQ for the instrument were calculated on each element's standard deviation obtained from the analysis  
217 of instrument carrier solution (Table S2 - supplementary materials). The lowest LOD parameter value were the ones of  
218 Eu, Tm and Lu with 0.017 ng mL<sup>-1</sup>, 0.019 ng mL<sup>-1</sup> and 0.013 ng mL<sup>-1</sup> respectively. The highest one is reported for Nd  
219 with 0.170 ng mL<sup>-1</sup>.

220 LOD and LOQ for the process were checked trough the analysis of acid mixture used for every sample mineralization  
221 (Table S2). Elements like Gd, Ho and Yb have LOD low values of 0.017 ng mL<sup>-1</sup>, 0.011 ng mL<sup>-1</sup> and 0.021 ng mL<sup>-1</sup>  
222 respectively. LOD and LOQ values for Tm under detectable limit.

223 Linearity. REE calibration curve was realized with CMS-1 stock standard solution on 8 points in parts per trillion  
224 (ppt): 0.1 ppt, on 0.25 ppt, 0.5 ppt, 1.0 ppt, 5.0 ppt, 10 ppt, 25 ppt and 50 ppt. In table S2 it's reported each element  
225 analysed for ultra-trace analysis, with its relative isotope, instrument operation mode and correlation coefficient (*R*<sup>2</sup>)  
226 resulted, in a range of calibration between 0.1 and 150 ng mL<sup>-1</sup>. Clearly each element analysed presented high correlation  
227 coefficient, especially Pr, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu, whose correlation coefficient was 1.000.

228 Accuracy parameters was validated with each element concentration recovery from SRM-1573A utilization with  
229 spiked standard addition of CMS-1 stock standard solution. In order to check the efficiency of the analysis for REE  
230 elements, for recovery calculation were taken in consideration the concentrations added with the spiked standard, since  
231 ultra-trace elements concentrations in SRM were indicative and not suitable for an accurate measure. In table S2 are listed  
232 the percentages of elements recovery and their RSD to each element with its relative isotope. All the REE elements were  
233 fully recovered. Furthermore, percentages above 100% indicate the low concentration in SRM-1573A that was certified  
234 just for consultation purpose.

235 Repeatability was checked with the repetition of same analysis with three replicate each. SRM-1573A with spiked  
236 standard addition were digested and analysed five times. Results are reported in table S2 through the main concentration  
237 obtained expressed in ng L-1 and RSD in percentage. Around 40 ppt of each REE was introduced with the spiked standard  
238 addition. The mean concentration reported indicates a satisfactory mean concentration calculated from the five repetitions.

239 Inter-day repeatability parameter validation was realized preparing the same sample used for repeatability but within  
240 three days. Each day a new analysis was conducted. Results are shown in table S2. Taking in consideration the  
241 concentration contribution of the spiked standards, data reported mean not only solid reliability due to results repetition  
242 but also substantial consistency regarding value obtained.

243

### 244 3.3. EVO oil samples multi-element trace and REE analysis

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246 To better visualize all multi-element and REE sample fingerprint results given, all the samples were grouped in four  
247 geographical zones: Central Italy, South Italy, Albany, and commercial COOP samples to characterize EVO oil from the  
248 different geographical areas. Central Italy includes Tuscany, Marche, and Liguria, while South Italy refers to Abruzzo,  
249 Calabria, Campania, Apulia, and Sardinia.

250 Generally, the EVO oil from the south of Italy has higher value of multi-element and REE respect to the EVO oil  
251 from Central Italy (120 ppb and 40 ppb respectively for multi-element and 40 ppt and 25 ppt respectively for REE), as  
252 shown in Figure 2. Two samples of Albany EVO oil were analysed to have an idea of a foreign oil's mineral composition.  
253 It appears similar to mineral fingerprint obtained with Italian ones.

254 In detail, Figure 2a reports the multi-element results for Central Italy. Iron is the element most present (with a  
255 maximum value of 39.523 ppb), followed by P, Ca, Al and K. Besides their toxicological and nutritional importance,  
256 metals play an important role in the stability of olive oils and the presence of Fe, Cu, Cr and Mn was observed in various  
257 studies. All the samples collected in Central Italy show similar value, except for Fe and Ca, that are higher than those  
258 described by Beltrán et al. (2015) or Sayago et al. (2018). Also, Na and K value are higher respect to those described by  
259 Camin et al. (2010) or Zeiner et al. (2010), except for the Liguria EVO oil sample. On the other hand, levels of toxic  
260 elements such as As, Cd, Ni and Pb are significantly lower than those reported in other works (Camin et al., 2010, Zeiner  
261 et al., 2010; Karabagias et al., 2013, Sayago et al., 2018). Observing the EVO oil collected in Tuscany but from different  
262 years (2013 and 2014 in Fig. 2a), it is important to note that the sample from 2014 shows higher level of all the elements  
263 respect to sample from 2013, except for Ca, Cr and Zn. In addition, the concentration of Fe in the 2014 sample is the  
264 highest of all the other samples from the Central Italy (39.523 ppb, as previously described). The Fe data obtained are  
265 similar to than those reported by Cabrera-Vique et al. (2012), who found Fe concentrations between 3.350 and 66.470  $\mu\text{g}$   
266  $\text{kg}^{-1}$  from Granada, Andalusia, Spain in virgin olive oils, but lower than those reported by Mendil et al. (2009) on olive  
267 oil from Turkey ( $\text{Fe} = 139.0 \pm 10.1 \mu\text{g g}^{-1}$ ) and by Zeiner et al. (2010) on virgin olive oil from Croatia ( $\text{Fe} = 1.81 \pm 1.76$   
268  $\mu\text{g g}^{-1}$ ). These authors explained that these differences between elements content could be attributed to the geographical  
269 origin (Cabrera-Vique et al., 2012) and could be used for their local characterization. Other authors hypothesize that this  
270 difference may originate from fertilizers or contamination during processing and storage (Gouvinhas et al., 2016). Liguria  
271 EVO oil is the one that shows the lowest values in all elements (Fig. 2a).

272 Figure 2b illustrates ultra-trace REEs main composition of Central Italy samples. Ce, La and Nd are the most present  
273 element in the ultra-trace elements of EVO oil samples and the Liguria EVO oil (coloured in green in Fig. 2b) is the  
274 sample with the highest values of trace elements.

275 If compared Figure 2a with Figure 2c, it's noticeable how multi-element concentration levels are higher in EVO oils  
276 of South Italy (Fig. 2c), reaching elevated concentration for Fe with a maximum value in Abruzzo (2017) sample with  
277 111.840 ppb. Apparently, the EVO oil samples from the south show a concentration more similar to each other, but the  
278 scale changes (here 120 ppb). The EVO oil samples from the south different, in fact, from each other in the concentration  
279 of Fe, Ni (Benincasa et al., 2007) but also in Al and K. Concentrations of Na found in these samples are in the range of  
280 1.754 ppb (Sardinia) – 10.764 ppb (Calabria) which is similar to that found in Zeiner et al. (2010), Beltrán et al. (2015)  
281 or Benincasa et al. (2012) but 50 times lower than the levels reported in Portuguese olive oils (Gouvinhas et al., 2016).  
282 The concentrations of Mn measured is lower than 1 ppb, which is 10 times lower than those of olive oils from five  
283 different geographic regions of central and southern Italy (Rossano, Andria, Lamezia, Spoleto and Pescara) (Benincasa  
284 et al., 2007) and 100 times lower than that previously reported in Benincasa et al. (2012), but in a similar range than those  
285 of Italian olive oils from Sicily and Tuscany (Camin et al., 2010). Also in this samples, levels of toxic elements such as  
286 As, Cd, Ni and Pb are significantly lower than those reported in other works, as previously described. Observing the EVO  
287 oil samples collected in Campania but from different years (2015a, 2015b and 2017), it is important to note that the sample  
288 from 2017 shows higher level of the majority of the elements respect to sample from the two others, except for Na and  
289 Al, which show doubling values compared to those of 2017. In addition, the Calabria EVO oil sample collected in Crotona  
290 (2015a) shows high value of all the elements respect to the EVO oil samples collected in Castrovillari (2015b) and  
291 Rossano (2015c). Finally, in the Apulia samples no remarks are observed.

292 Also, for Figure 2d, it's easily noticeable how lanthanides concentration is higher for South Italy samples, reaching  
293 the highest values for two Calabria samples (2015a and 2015c, coloured in orange and yellow respectively).

294 The samples from Albany should have had similar concentrations, since the EVO oil was produced in same mill,  
295 from the same olives and plants. The 2014 EVO oil sample shows higher values in K, Ca, Fe, Ni, Zn, while the 2015  
296 EVO oil sample in Na, Mg, Al, P and Sr (Fig. 2e). Generally, the Albany samples appear similar in concentration value  
297 to EVO oil sample from central Italy, but with the highest value of Ca as for other EVO oil samples from south of Europe,  
298 as for example in Spain (Sayago et al., 2018), Croatia (Zeiner et al., 2010), Greek (Karabagias et al., 2013).

299 As for multi-element analysis, the two samples from Albany appear similar in concentration value to EVO oil sample  
300 from Central Italy. Also in this case, the two Albany EVO oil samples show differences in the majority of the REE  
301 elements, but generally, the samples collected in 2015 has higher value respect to the sample collected in 2014 (Fig. 2f).

302 The three samples from COOP production show similar concentration of the central Italy and of the Albany EVO oil  
303 samples, with a maximum value of P and Fe around 30 ppb (Fig. 2g). Al and Ca are also present as for all other EVO oil  
304 samples.

305 The two COOP Fiore samples show similar value to each other for REE elements, this could confirm similar  
306 provenance (Fig. 2h). Different value, on the other side, has the EVO oil sample COOP Costanza, probably from different  
307 origin. Generally, REE values in COOP FIORE are similar to those from the Central Italy (except for the EVO oil from  
308 Liguria). The opposite is for the EVO oil COOP Costanza, which shows similar value on the EVO oil samples collected  
309 in Central Italy. Nevertheless, results in Figure 2h are different from results in Figure 2g, where the two COOP Fiore  
310 EVOOs are significantly different in the content of Na, Al, Fe and Zn, while the COOP Costanza EVOO has more similar  
311 concentration to one of them. All these considerations could give us a good information related to the possible provenance  
312 of the Italian EVO oil COOP FIORE and Costanza.

313 Scientific researchers have been reported that the content in mineral is usually affected in practice by the agro-  
314 environmental conditions and the olive genetic diversity (Gouvinhas et al., 2016), which certainly reflects the origin of  
315 provenance. The content of trace metals in EVO oil is also an important criterion for the assessment of oil quality with  
316 regard to their influence on human nutrition and health. Contents of Ni, As, Cu, Fe, Cd and Pb in all the samples analyzed  
317 are given in table 2. Especially As, Cd and Pb are very important on their toxicity and metabolic role because they catalyze  
318 the decomposition of hydro-peroxides, aldehydes, ketones, acids, and epoxides (Yassin et al., 2021). These compounds  
319 could increase carcinogenic effect especially on the digestive system by reacting with proteins and pigments present in  
320 the food (Ghane et al., 2022).

321 Obtained results reveal that the highest detected content of Ni is registered in the Abruzzo 2017 EVO oil sample  
322 (28.971 ppb). Generally, the Apulia samples have high value of Ni, around 3 and 4 ppb. It is interesting to note that the  
323 Ni concentration in the same EVO oil but with different year of production show different value of this metal, for example  
324 Apulia with very different concentration of Ni and Tuscany 2013 and 2014 with Ni value 0.305 ppb and 2.517 ppb  
325 respectively. The sample Calabria 2015a came from Crotona and it shows higher value of contaminants respect to the  
326 other Calabria samples collected in the same year but in two small town respect to Crotona. This could be correlate to the  
327 higher pollution of the Crotona city that could affect the olive plant and consequently the oil. Instead of the Ni value of  
328 the two sample of Campania EVO oil is very similar. All these values are lower than other EVO oil samples, for example  
329 compared to the Iranian EVO oil (Ziarati et al., 2019). The highest content of As is registered in the Campania 2017  
330 sample, but generally with very low value in all the samples analyzed. Table 2 shows also the Cd content, for which the  
331 highest value is registered in the Campania 2017 sample as for As content, but also in this case lower than those other  
332 EVO oil samples (Ziarati et al., 2019). In addition, the highest Pb concentration is registered in Calabria 2015a and Apulia  
333 2016 samples (range around 1 ppb, lower than those other EVO oil samples (La Pera et al., 2002; Ziarati et al., 2019)).  
334 Finally, the concentrations of Cu measured is 0.35 ppb both for the samples collected to the north and to the south of  
335 Italy. This value is much lower than those previously reported in Argentine (Savio et al., 2014), Spain (Cabrera-Vique et  
336 al., 2012) and Italy too (Astolfi et al., 2021). Nevertheless, these results confirm that the contents of Ni, As, Cd and Pb in  
337 all the Italian samples analyzed not exceed the limits set by Codex Alimentarius and USDA (2001) and by the  
338 International Olive Oil Council (2009) related the legislated metals (As, Cu, Fe and Pb). The average contents of V in the  
339 EVO oil samples are 0.259 and 0.296 for the north samples and the south samples respectively and are significantly lower  
340 than in European EVO oil (Beltrán et al., 2015; Llorent-Martínez et al., 2011a; Pošćić et al., 2019) but also in the other  
341 Italian study, as in Astolfi et al. (2021), in which the average V value is equal to 0.52 in the Italian EVO oil samples.

342 By comparing our data with those of the other scientific research, generally, REE trace elements are detected in  
343 similar quantities than those previously reported by Sayago et al. (2018) and in greater quantity than those reported by  
344 Camin et al. (2010). Moreover, some correlations between REEs are found as shown in Figure 3, Ce, Nd and Gd are  
345 correlated in all samples analysed. Ce and Nd are also ones of the most REEs concentrated (Fig. 3a), with a maximum of

346 36.986 ppt and 14.938 ppt respectively in Calabria (2015c) sample. In addition, also La-Nd and La-Sm (Figs. 3d and 3e  
 347 respectively) have correlated each other but lower respect to the previous elements described.

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**Table 2.** Content of toxic metals in the various samples collected and analyzed by ICP-MS-QQQ, expressed in ppb.

Sample name	Ni	As	Cu	Fe	Cd	Pb
Albany 2014	0.140 x10	0.050	0.493	0.179 x 10 <sup>2</sup>	0.017	0.442
Albany 2015	0.217	0.127	0.277	0.158 x 10 <sup>2</sup>	0.000	0.006
Tuscany 2013	0.305	0.023	0.467	0.153 x 10 <sup>2</sup>	0.006	0.220
Tuscany 2014	0.251 x 10	0.009	0.375	0.395 x 10 <sup>2</sup>	0.002	0.468
Marche 2015	0.127 x 10	0.077	0.594	0.197 x 10 <sup>2</sup>	0.026	0.772
Liguria 2018	0.410	0.135	0.000	0.168 x 10 <sup>2</sup>	0.002	0.047
Abruzzo 2017	0.289 x10 <sup>2</sup>	0.082	0.445	0.111 x 10 <sup>3</sup>	0.004	0.180
Calabria 2015a	0.281 x 10	0.009	0.519	0.526 x 10 <sup>2</sup>	0.132	0.166 x 10
Calabria 2015b	0.563	0.000	0.457	0.148 x 10 <sup>2</sup>	0.051	0.618
Calabria 2015c	0.640	0.000	0.124	0.134 x 10 <sup>2</sup>	0.000	0.023
Campania 2015a	0.109 x 10	0.027	0.118	0.170 x 10 <sup>2</sup>	0.004	0.066
Campania 2015b	0.618 x 10	0.014	0.396	0.582 x 10 <sup>2</sup>	0.021	0.668
Campania 2017	0.885	0.431	0.353	0.145 x 10 <sup>2</sup>	0.308	0.435
Sardinia 2016	0.300	0.000	0.121	0.134 x 10 <sup>2</sup>	0.000	0.044
Apulia 2013a	0.327 x 10	0.032	0.456	0.206 x 10 <sup>2</sup>	0.009	0.382
Apulia 2013b	0.538	0.045	0.536	0.173 x 10 <sup>2</sup>	0.006	0.207
Apulia 2013c	0.174 x 10	0.073	0.222	0.248 x 10 <sup>2</sup>	0.004	0.130
Apulia 2014	0.350 x 10	0.023	0.238	0.233 x 10 <sup>2</sup>	0.000	0.522
Apulia 2016	0.233 x 10	0.005	0.529	0.414 x 10 <sup>2</sup>	0.049	0.147 x 10
Apulia 2018a	0.420 x 10	0.023	0.579	0.782 x 10 <sup>2</sup>	0.011	0.367
Apulia 2018b	0.359	0.200	0.159	0.125 x 10 <sup>2</sup>	0.132	0.129
Coop FIORE 2013	0.105 x 10	0.054	0.118 x 10	0.302 x 10 <sup>2</sup>	0.011	0.231
Coop FIORE 2014	0.487	0.049	0.000	0.123 x 10 <sup>2</sup>	0.002	0.032
Coop Costanza	0.156	0.077	0.000	0.126 x 10 <sup>2</sup>	0.004	0.031

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### 351 3.4. Multivariate analysis

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PCA was applied for a preliminary evaluation of data quality. In PCA analysis, eigenvalues represent the variance associated to the related principal component. The sum of all the eigenvalues is equal to the total variance of the data. Assuming that each eigenvalue < 1 is associated to the lowest relevant information, they could be eliminated without consequences. To do that, the first eight principal components with each eigenvalue, the variability (expressed in percent) and the cumulative variance (expressed in percent) are reported in table S3 (supplementary materials) and in the Scree Plot in Fig. S1 (supplementary materials) to graphically represent each component weight on the total variance. Table S3 reflects the quality of the projections from the N-dimensional initial table to a lower number of dimensions. First eigenvalue equals to 15.004 represents the 36.6% of the system variance. Observing PC1 and PC2 cumulative variance, the first two principal components represent 60.4% of the initial variability. PC1 represent the maximum variance, and being orthogonal with PC2 for construction, is uncorrelated with it. PC2 represents the maximum residual variance. Scree plot graphs eigenvalues in function of PC's number (Fig. S1). The selection of PCs is made according to a sharp decrease of the curve to the horizontal asymptote. The distinction of the first two PCs is already graphically clear compared to the following others.

Then, to analyse graphically the variables' role, a PCA loadings plot is required. In Figure S2 (supplementary materials) a correlation circle is reported, which described not a confidence interval but a plot of the correlation between the variables and the principal components (PC1 and PC2). Horizontal axis represents PC1 and vertical axis PC2, while the red vectors reflect the investigated variables. According to the length of each vector, it's explained the

370 representativeness quality in the investigated PCA dimensions; longer a vector is more it's represented by these two  
371 principal components. The shortest ones might be better explained from other factors (Popović et al., 2020). REEs are  
372 well represented from PC1 reporting La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. REEs form a right  
373 angle with some of the contaminants well represented from PC2, denoting that are uncorrelated to each other.  
374 Contaminants reported in PC2 axis are Cd, As, V, Ba, Tl, Th and U. This is more important, because these contaminants  
375 generally enter into the soil agro-ecosystem through natural processes and anthropogenic activities (Li et al., 2019;  
376 Mng'ong'o et al., 2021). In detail, Cd is one of the toxic metals most monitored, due to its relevant consequences on human  
377 health, and it is transferred to food through fertilizers, in particular the ones based on P, and through packaging systems  
378 (Osman et al., 2019). The concentration of Cd in phosphate fertilizers is an issue of great concern and its allowed amount  
379 has been continuously discussed by European Commission (Ulrich, 2019); its presence has been found in phosphoric  
380 pentoxide due to Cd trace concentration in the phosphate rock used for their manufacture (Zheng et al., 2020; Liu et al.,  
381 2021). Almost all phosphate fertilizers are produced from phosphate rock (El-Bahi et al., 2017). Moreover, Cd  
382 contamination from fertilizers is mainly accumulated in crop-production soil and its accumulation might be higher in  
383 south Mediterranean soils, where rains are less frequent, thus obstructing its leaching (Nardi et al., 2017; El-Sherbiny and  
384 Sallam, 2021). In Fig. S2, Cd is relevant in the analysis of the PCA loadings plot. Knowing the low contamination on the  
385 geographically sampling site not so close to important route (except only for one site), the high value of this contaminant  
386 could be related to agronomic practices through the use of phosphate fertilizers (Dharma-wardana, 2018; Schaefer et al.,  
387 2020). Another element that can be introduced easily into food chain is As, whose distribution has been defined from  
388 European Food Safety Authority mostly present in food commodities and current water (European Food Safety Authority,  
389 2014) and it could be present in some pesticide's composition (Osman et al., 2019). In pesticides also Ba is traceable. In  
390 Fig. S2, As and Ba, as for Cd previously described, are relevant in the analysis of the PCA loadings plot. This could  
391 confirm a possible pollution by aggressive agronomic practices. Additionally, V is accumulated in soil composition, and  
392 it may cause a serious damage for crop cultivations, even if it is naturally present also into plant's tissues (Li et al., 2020).  
393 The diffusion of V into the atmosphere and subsequently its deposition in soil, is often due to anthropic reasons, since it  
394 is mainly released from oil's products combustion and from activities related to steel industry. Vanadium's anthropic  
395 emissions exceed natural ones by a factor of 1.7 (Schlesinger et al., 2017). In the PCA loadings plot of Fig. S2, V is not  
396 so important as the previous contaminants, but its presence adds importance to the possibility of anthropic contamination  
397 (Beltrán et al., 2015). These elements differed from metals like Ni, Cu, Zn and Pb, whose concentrations were constant  
398 in EVO oil samples. Moreover, at low concentrations toxic metals like Ni, Cu and Zn are micro-elements essential to the  
399 metabolic role and the reproduction of plants, animal, and humans (Hussain et al., 2020).

400 On the other hand, PCA score plot reports the separation among the EVO oil samples in relation to quality, cultivar,  
401 and processing method. Figure S3 (supplementary materials) presents the graphic distribution of the EVO oil samples in  
402 relation to the geographically origin, according to the first two principal components scores (PC1 and PC2). Each point  
403 of the graph is coloured according to their provenance origin. Most of the EVO oil samples are grouped in the lower part  
404 of the graph, except for the sample from Campania (Perdifumo – SA, 2015) and Apulia (Molfetta – BA, 2018b). The  
405 EVO oil samples from Calabria and Albany follow a different trend: the two samples of Albany seem to be in two different  
406 quadrants, even if always in the lower part of the graph (2014 in the left part and 2015 in the right part); while the EVO  
407 oil samples of Calabria, as well as being in different quadrants, are also found in different positions with respect to the  
408 zero of both PC1 and PC2. Finally, the sample of Liguria is found together with a sample of the Campania (Valturara –  
409 AV, 2017) and the two remaining ones of Calabria (Crotona – CR, 2015a and Rossano – CS, 2015c) in the upper right  
410 quadrant (opposite quadrant with respect to the quadrant in which most of the samples are found). A particular case is  
411 that of Sardinia, which together with a sample of Campania (Pimonte – NA, 2015) are found in the central part of the  
412 graph, where the 0 vectors of both PC1 and PC2 intersect. The graph in figure S3 allows discriminating EVO oil samples  
413 on the basis of the graphic distribution of the EVO oil samples in relation to the geographically origin, according to the  
414 elements quantify by the ICP-MS-QQQ analysis. EVO oil samples from the same geographical origin are very closed to  
415 each other, except for the Campania EVO oil samples, and especially for the two Campania EVO oil samples collected  
416 in the same place but in different years. This could be an important base for future study, to better characterize the  
417 sampling area to know change on soil or on plant maybe in relation to climate change or to different use of fertilizer.

418 To complete PCA analysis, a biplot is reported in Figure 4. The cluster in the negative side of PC1 and PC2 (on the  
419 left bottom of the graph in Fig. 4) represents samples characterized by high value of the general elements present in an  
420 EVO oil samples, as Zn, Cu and mostly Fe, as we expected (Martinez et al., 2018). In the biplot it's clear how two samples  
421 fall back into the contaminants area having higher concentrations of toxic elements compared to the others (Campania,  
422 Perdifumo – SA, 2015; Apulia (Molfetta – BA, 2013c). In the ones reported in the axis related to REEs elements are  
423 samples that stand out of the crowd for their particular high definition of ultra-trace composition of rare earth elements.

424 Regarding the three industrial olive oil samples, the two COOP Fiore (2013 and 2014) are very similar to most of the  
425 samples analysed. On the opposite, COOP Costanza is in the same part of the figure of Calabria and Liguria samples, but  
426 with higher value of REE elements.

427

#### 428 4. Conclusion

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This work focused on the research of a reliable method to analyse many EVO oil samples from different areas.

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432 Fundamental steps of this method's development were sample's mineralization and sample's analysis. For the first  
433 one different acid mixtures were tested in order to use the minimum quantity of acid having at the same time a clear  
434 solution without any organic matrix dispersed in the solution. For the analysis step different dilutions were tested in order  
435 to obtain a sample reading suitable with a calibration curve calculated to contain each element's range of concentration.  
436 Moreover, the method developed was successfully validated according to some parameters that must be optimized to  
realize a reliable method: linearity, accuracy, LOD and LOQ, repeatability and inter-day repeatability.

437

438 In addition, using the triple quadrupole ICP-MS in a Clean Room ISO 6 significantly lowers the LODs of each  
439 elements analysed. This makes it possible to quantify even very low values or closed to the LOD, especially of REE,  
which can be excellent markers for identifying the fingerprint.

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441 Good results were obtained both for trace multi-element analysis and for ultra-trace REE analysis as we expected.

442

443 Both trace and ultra-trace elements show changes between the analysed samples. At the end, with data obtained from trace (ppb) and ultra-trace (ppt) analysis a PCA was conducted to start pointing  
444 out a possible and continuative study on the relationship between EVO oil samples, originating from different areas.

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## Supplementary materials

**Table S1.** LOD and LOQ of the instrument and of the process for multi-element trace analysis, expressed in ng mL<sup>-1</sup>; linearity of the external calibration for multi-element trace analysis; accuracy determination through SRM-1573A recovery and spiked standard additions; repeatability and inter-day repeatability of the multi element trace analysis. Symbol \* represent element read at the higher dilution; symbol ° represent element read at (1:100) dilution.

Element	Instrument		Process		Linearity		Accuracy		Repeatability		Inter-day repeatability (ng mL <sup>-1</sup> )					
	LOD	LOQ	LOD	LOQ	Mode	R2	Recovery (%)	RSD (%)	Mean Concentration	RSD (%)	Day 1	RSD (%)	Day 2	RSD (%)	Day 3	RSD (%)
<sup>9</sup> Be*	0.006	0.020	0.004	0.0152	No Gas	1.000	86.1	3.9	13.726	0.067	16.288	0.5	16.036	1.0	16.304	0.1
<sup>11</sup> B	0.208	0.693	0.145	0.483	No Gas	0.9996	92.3	1.3	15.010	0.732	16.147	1.0	17.107	0.9	16.189	1.4
<sup>23</sup> Na	0.012	0.052	0.281	0.935	No Gas	0.9997	87.5	1.4	17.153	0.778	16.220	0.9	19.190	0.7	16.807	1.0
<sup>24</sup> Mg°	0.122	0.407	0.133	0.443	He	0.9999	106.2	2.3	38.924	0.217	56.856	4.2	52.628	0.3	55.579	2.5
<sup>27</sup> Al	2.170	7.232	0.875	2.918	No Gas	0.9999	90.2	3.9	28.468	0.616	22.024	0.8	23.041	5.4	28.903	2.0
<sup>31</sup> P	1.520	5.065	1.440	4.796	No Gas	0.9998	98.7	5.7	44.122	0.009	53.490	0.7	53.911	1.5	54.720	0.7
<sup>39</sup> K°	0.730	2.432	1.370	4.566	No Gas	0.9998	114.3	0.3	93.789	0.225	161.800	1.1	126.999	1.4	134.759	1.4
<sup>44</sup> Ca°	0.819	2.730	1.192	3.976	He	0.9995	77.2	1.7	28.750	0.717	43.159	6.1	35.685	2.9	40.391	4.3
<sup>51</sup> V*	0.213	0.710	0.144	0.479	No Gas	0.9999	95.5	1.3	15.194	0.122	17.741	2.1	16.967	1.1	17.520	1.2
<sup>52</sup> Cr*	0.049	0.162	0.061	0.203	No Gas	0.9998	93.2	1.3	14.865	0.059	17.202	0.3	16.878	1.3	17.040	0.1
<sup>55</sup> Mn	0.018	0.061	0.009	0.029	No Gas	0.9999	109.3	1.2	18.048	0.066	20.922	0.5	20.667	1.2	21.017	0.6
<sup>56</sup> Fe	0.520	1.730	0.460	1.533	No Gas	0.9995	110.6	3.1	21.994	0.217	24.514	1.8	23.625	1.3	24.938	0.5
<sup>59</sup> Co	0.001	0.003	0.004	0.015	No Gas	0.9999	91.3	6.0	14.685	0.030	16.966	0.3	16.574	0.1	16.772	1.3
<sup>60</sup> Ni*	0.040	0.130	0.164	0.550	He	0.9999	93.9	1.5	14.962	0.093	17.444	1.5	16.423	3.0	17.457	1.5
<sup>63</sup> Cu*	0.012	0.041	0.070	0.232	No Gas	0.9997	89.4	1.0	14.295	0.008	16.607	0.4	16.231	0.6	16.547	0.4
<sup>66</sup> Zn*	0.392	1.310	0.300	0.993	He	0.9999	62.6	4.6	9.771	0.346	15.809	0.6	15.284	4.6	15.629	3.4
<sup>69</sup> Ga*	0.005	0.015	0.044	0.148	He	0.9999	94.0	1.5	15.021	0.037	16.838	1.5	16.980	1.6	17.360	2.0
<sup>75</sup> As*	0.100	0.332	0.427	1.423	He	0.9999	92.0	2.9	14.674	0.075	16.459	4.6	15.790	2.7	16.169	1.0
<sup>78</sup> Se*	0.338	1.126	0.173	0.575	No Gas	0.9999	82.9	4.9	13.172	0.134	15.538	2.6	16.191	3.1	15.397	3.7
<sup>85</sup> Rb	0.019	0.065	0.035	0.120	He	1.0000	104.9	3.8	14.875	0.093	17.191	1.0	16.767	0.5	16.994	2.9
<sup>88</sup> Sr	0.029	0.098	0.073	0.244	He	0.9999	106.9	1.0	15.674	0.160	18.241	2.1	18.441	1.4	18.328	0.2
<sup>107</sup> Ag*	0.001	0.005	0.002	0.008	No Gas	0.9998	61.7	0.6	9.869	0.001	16.608	0.5	16.214	0.7	16.517	0.6

<sup>111</sup> Cd	0.040	0.129	0.025	0.082	He	1.0000	81.0	3.3	14.497	0.123	16.350	1.6	16.718	2.2	16.821	3.4
<sup>133</sup> Cs*	0.004	0.015	0.002	0.008	No Gas	0.9999	93.1	1.3	14.850	0.074	17.050	1.1	16.751	0.2	16.999	0.9
<sup>137</sup> Ba	0.109	0.365	0.160	0.526	He	0.9998	98.8	0.5	15.205	0.127	17.837	3.9	18.407	3.3	17.749	3.3
<sup>205</sup> Tl	0.002	0.006	0.002	0.005	No Gas	0.9998	85.6	0.7	13.682	0.030	15.728	0.8	15.482	0.2	15.736	0.7
<sup>208</sup> Pb*	0.028	0.094	0.062	0.208	No Gas	0.9998	86.5	1.8	13.772	0.088	15.942	1.0	15.650	0.5	15.773	0.2
<sup>232</sup> Th*	0.025	0.083	0.030	0.098	No Gas	1.0000	88.5	0.5	14.085	0.099	16.189	0.9	15.935	0.7	16.108	0.7
<sup>238</sup> U*	0.001	0.004	0.002	0.005	No Gas	1.0000	88.5	0.7	13.888	0.033	17.037	1.9	16.404	3.5	16.096	1.4

**Table S2.** LOD and LOQ of the instrument and of the process for the rare earth elements (REE) ultra-trace analysis, expressed in ppt (n.d. means under detectable limit); linearity of the external calibration for the rare earth elements ultra-trace analysis (ppt); accuracy determination through SRM-1573A recovery and spiked standard additions; repeatability and inter-day repeatability of the rare earth elements ultra-trace analysis.

Element	Instrument		Process		Linearity		Accuracy		Repeatability		Inter-day repeatability (ppt)					
	LOD	LOQ	LOD	LOQ	Mode	R2	Recovery (%)	RSD (%)	Mean Concentration	RSD (%)	Day 1	RSD (%)	Day 2	RSD (%)	Day 3	RSD (%)
<sup>139</sup> La	0.042	0.140	0.136	0.454	O <sub>2</sub>	0.9999	104.3	1.7	42.303	1.7	42.069	2.1	41.475	2.2	41.705	1.7
<sup>140</sup> Ce	0.042	0.141	0.093	0.311	O <sub>2</sub>	0.9999	100.7	2.6	41.646	2.5	41.444	2.8	40.785	2.7	40.291	2.6
<sup>141</sup> Pr	0.041	0.138	0.105	0.350	O <sub>2</sub>	1.0000	105.7	2.3	42.786	1.6	42.689	0.6	41.958	2.1	42.302	2.3
<sup>146</sup> Nd	0.170	0.568	0.469	1.565	O <sub>2</sub>	0.9999	106.2	1.9	43.096	1.8	42.852	3.7	42.063	2.4	42.508	1.9
<sup>147</sup> Sm	0.107	0.356	0.207	0.690	O <sub>2</sub>	1.0000	103.9	2.7	42.583	2.3	42.860	2.5	41.512	1.5	41.544	2.7
<sup>153</sup> Eu	0.017	0.057	0.032	0.107	No Gas	1.0000	106.9	0.3	43.238	2.0	43.599	0.5	42.055	2.2	42.776	0.3
<sup>157</sup> Gd	0.068	0.228	0.017	0.057	O <sub>2</sub>	1.0000	105.1	3.0	42.340	1.3	43.235	2.5	41.690	0.6	42.054	3.0
<sup>159</sup> Tb	0.067	0.225	0.119	0.396	No Gas	0.9998	106.2	7.4	41.926	2.0	42.645	7.0	41.644	1.3	42.494	7.1
<sup>163</sup> Dy	0.021	0.071	0.066	0.220	O <sub>2</sub>	1.0000	106.2	2.9	43.241	1.7	42.748	2.1	42.673	1.7	42.483	2.9
<sup>165</sup> Ho	0.036	0.012	0.011	0.037	O <sub>2</sub>	1.0000	105.9	3.2	42.950	1.6	43.253	0.8	42.131	2.0	42.355	3.2
<sup>166</sup> Er	0.061	0.202	0.068	0.228	O <sub>2</sub>	1.0000	106.9	1.6	42.816	2.0	42.294	2.4	41.403	1.7	42.759	1.6
<sup>169</sup> Tm	0.019	0.062	n.d.	n.d.	O <sub>2</sub>	1.0000	106.4	1.0	43.046	1.7	43.187	0.4	41.900	2.0	43.383	0.9
<sup>172</sup> Yb	0.049	0.164	0.021	0.070	No Gas	1.0000	105.6	0.5	43.004	1.3	43.501	1.1	42.854	1.1	42.039	0.9
<sup>175</sup> Lu	0.013	0.045	0.650	2.166	O <sub>2</sub>	1.0000	106.4	1.1	43.258	2.0	43.431	1.6	42.267	1.9	42.457	1.1

**Table S3.** Eigenvalues and cumulative variance (expressed in percentage) of the data obtained by ICP-MS-QQQ on EVO oil samples.

Principal Component	Eigenvalue	Variability (%)	Cumulative variance (%)
PC1	15.004	36.596	36.596
PC2	9.770	23.828	60.424
PC3	4.057	9.894	70.319
PC4	3.215	7.841	78.160
PC5	2.061	5.027	83.188
PC6	1.842	4.492	87.679
PC7	1.041	2.539	90.218
PC8	0.912	2.224	92.442

**Figure S1**

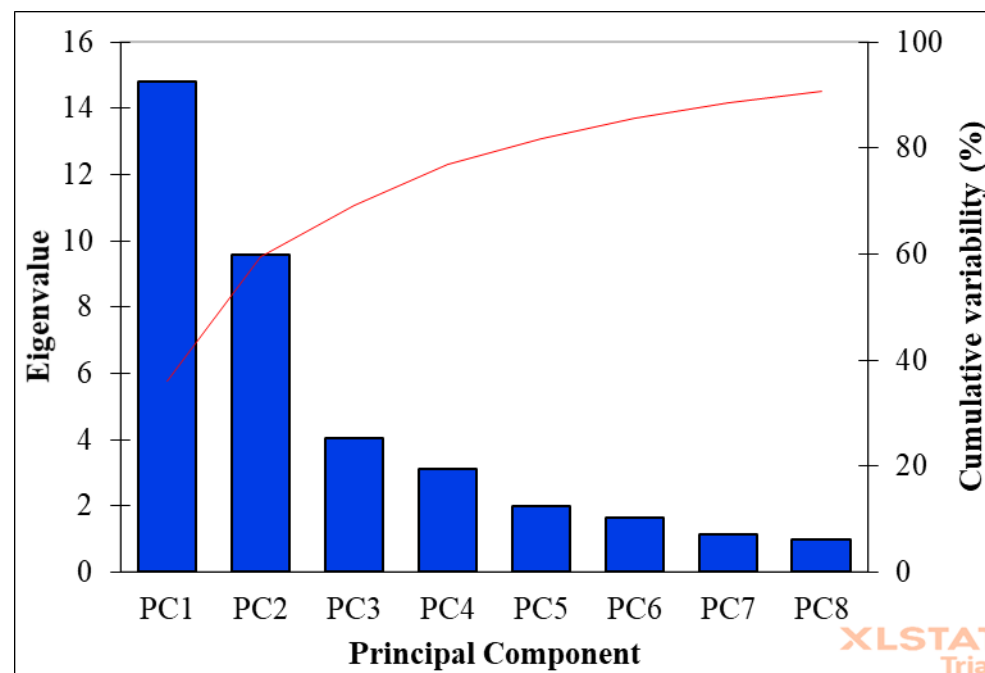


Figure S2

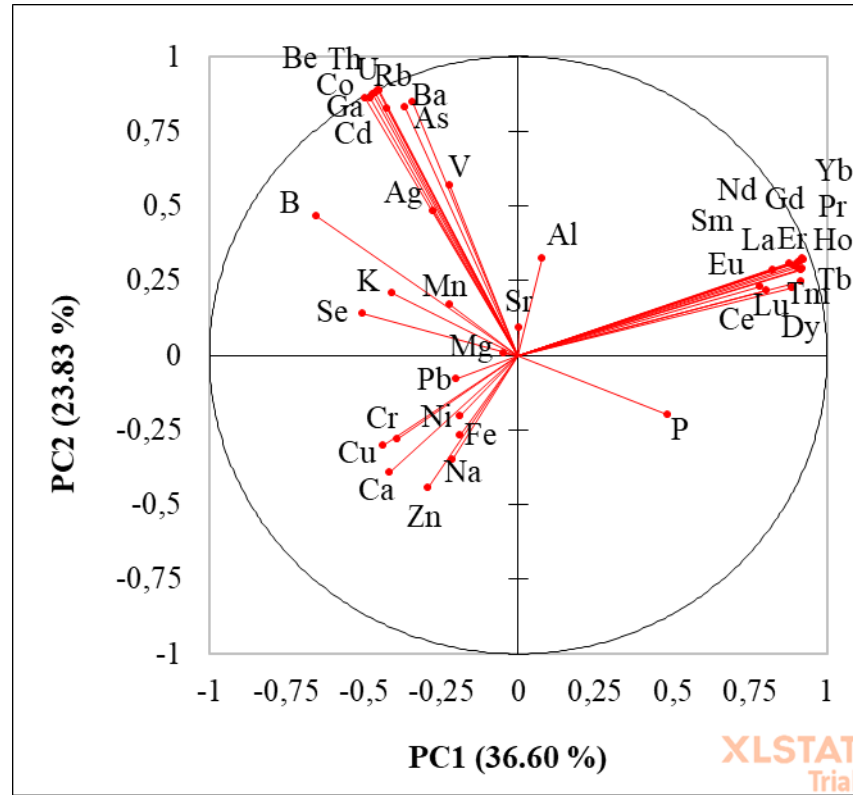
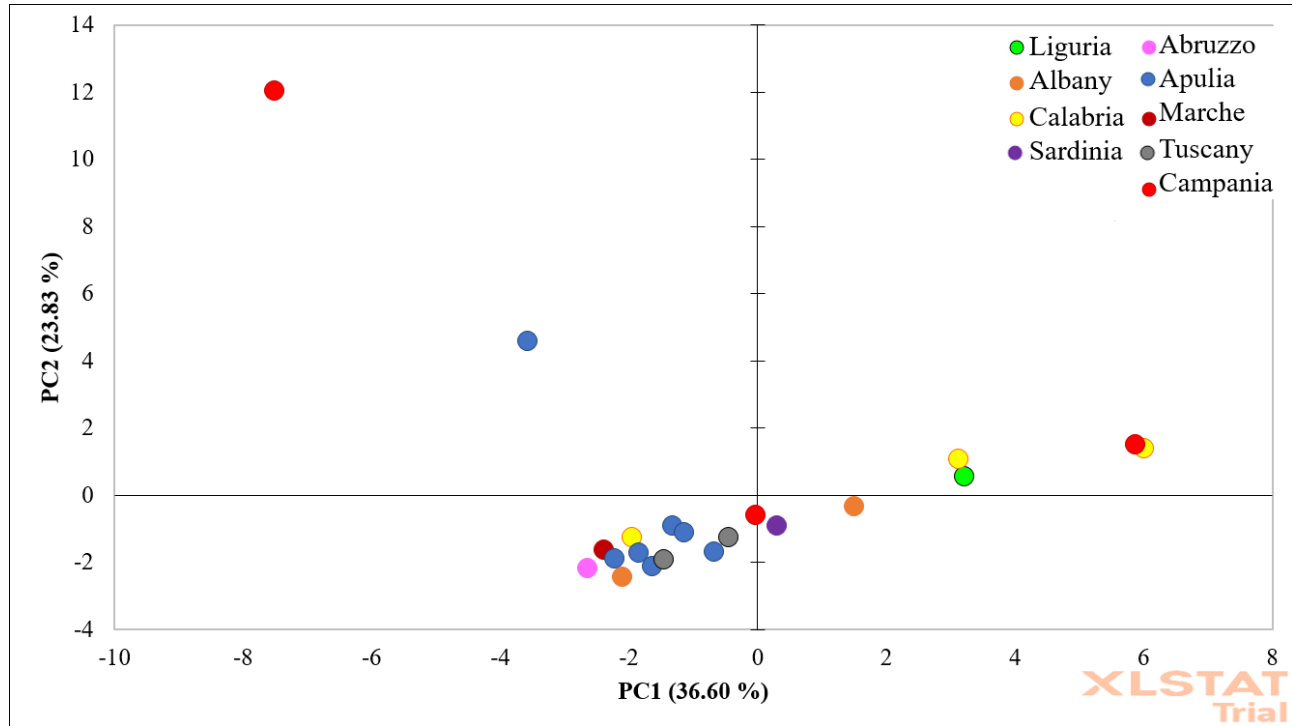


Figure S3



## Figure captions

**Figure 1.** Extra Virgin Olive (EVO) oil sampling sites. On the right, some EVO oil after sampling collection.

**Figure 2.** Multi-element and REE ultra-trace data representation for EVO oil samples, expressed in ppb and ppt respectively: a) multi-element in Central Italy; b) REE in Central Italy; c) multi-element in South Italy; d) REE in South Italy; e) multi-element in Albany; f) REE in Albany; g) multi-element in COOP olive oil; h) REE in COOP olive oil.

**Figure 3.** REE regression in all the EVO oil samples, expressed in ppt, between a) Ce-Nd; b) Gd-Nd; c) Gd-Ce; d) La-Nd; e) La-Sm.

**Figure 4.** Principal Component Analysis (PCA) biplot of the EVO oil data obtained by ICP-MS-QQQ and analysed by XLstat Addinsoft. In black the three industrial olive oil samples. The red vectors reflect the investigated variables.

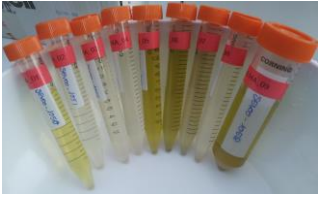
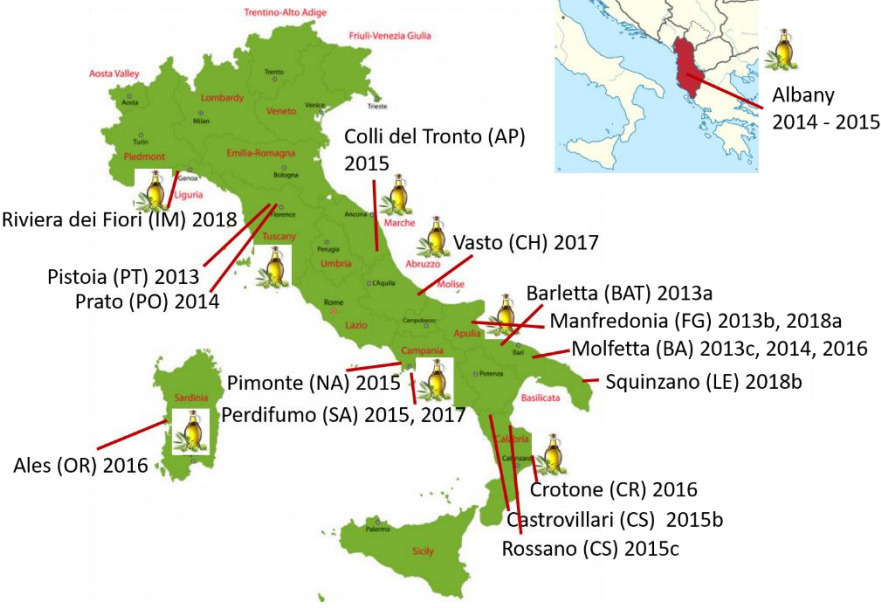
**Figure S1.** Scree plot related to Table S3 (supplementary materials), obtained with XLstat Addinsoft.

**Figure S2.** Principal Component Analysis (PCA) loadings plot of the EVO oil data obtained by ICP-MS-QQQ and analysed by XLstat Addinsoft. The red vectors reflect the investigated variables.

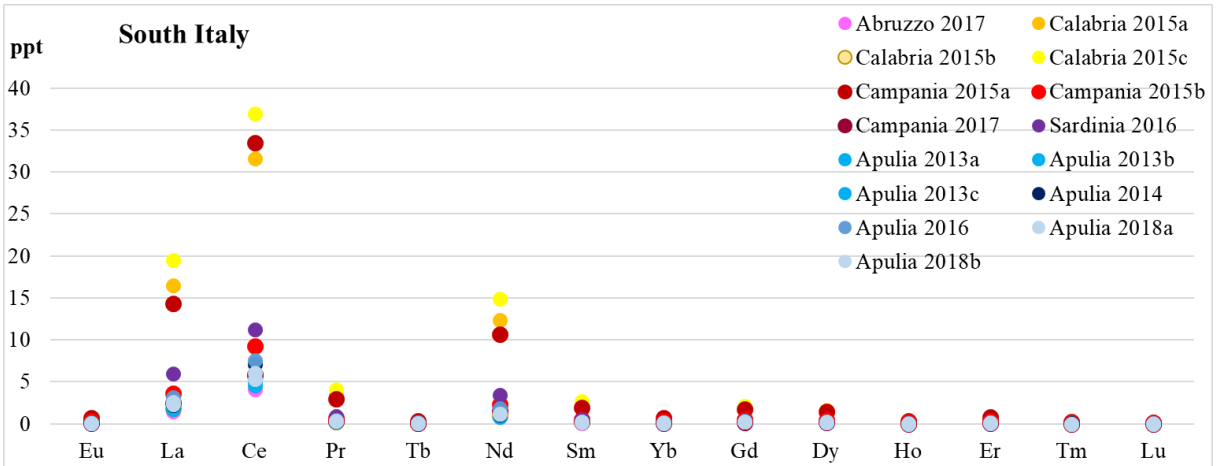
**Figure S3.** Principal Component Analysis (PCA) score plot of the EVO oil data obtained by ICP-MS-QQQ and analysed by XLstat Addinsoft.

**Figures**

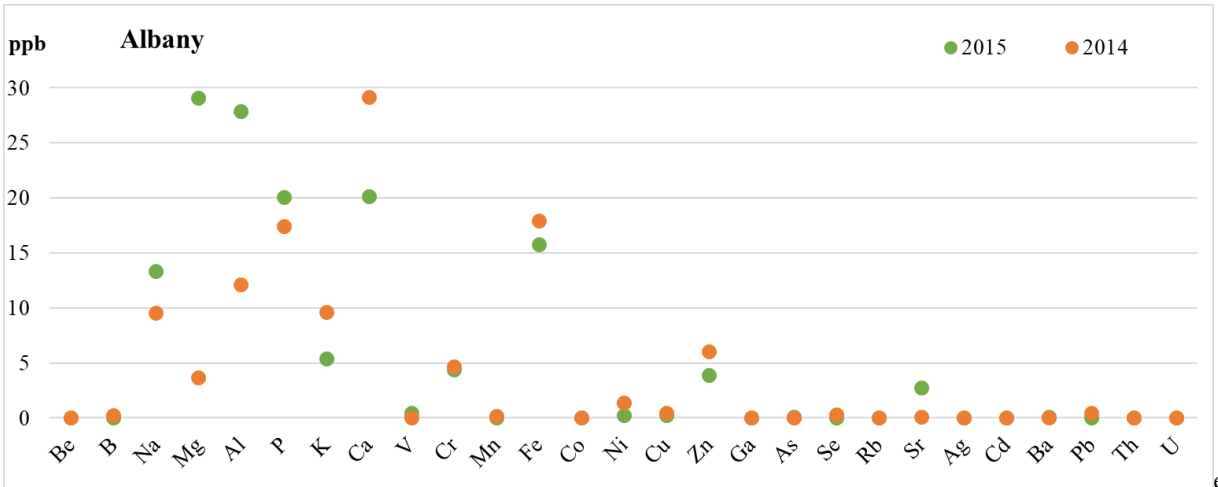
**Figure 1**



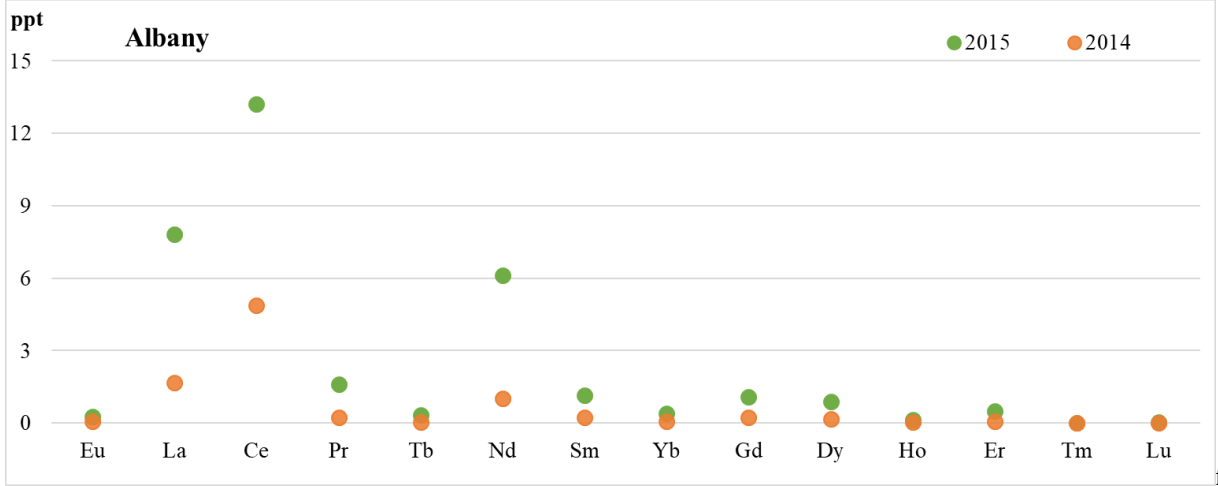




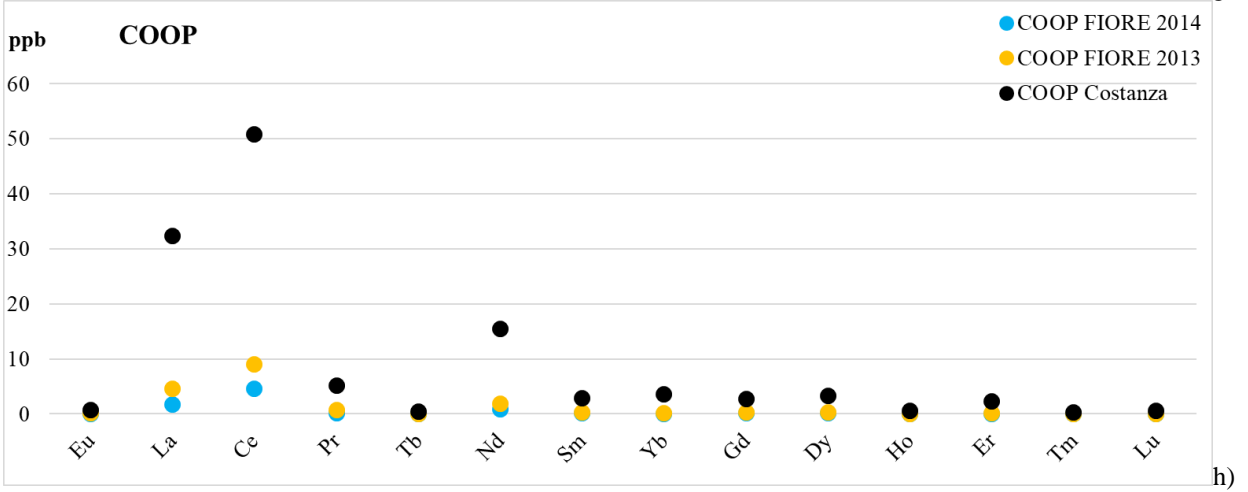
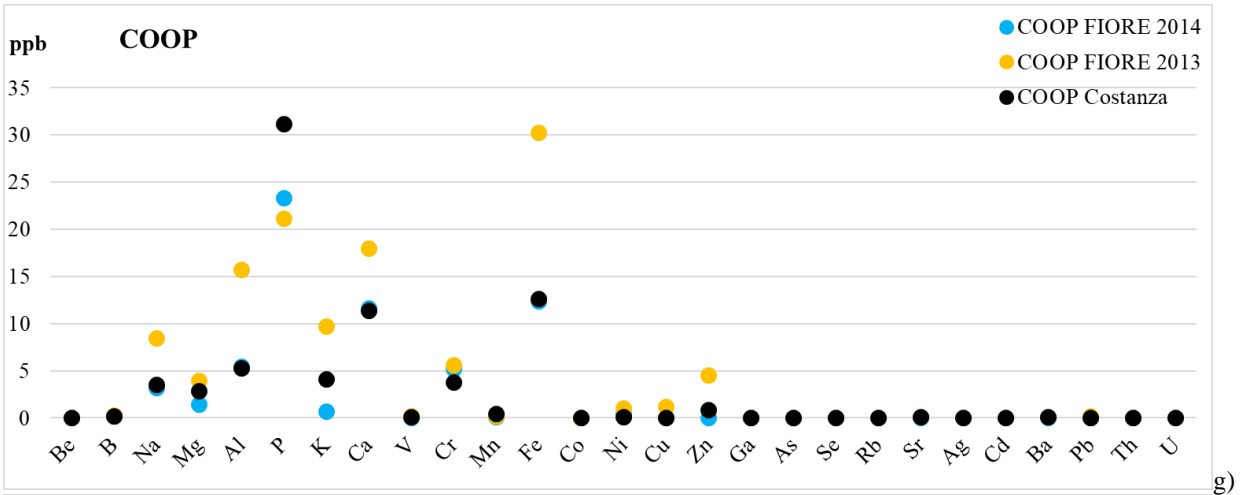
d)



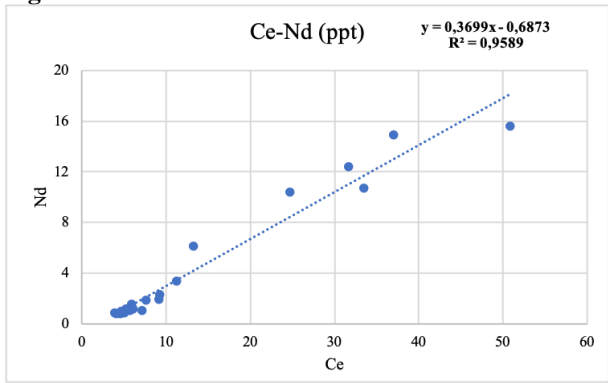
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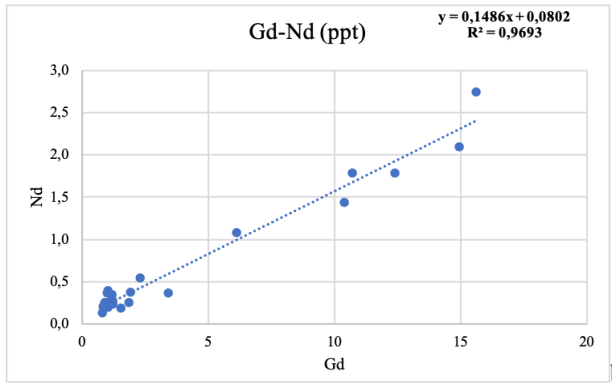
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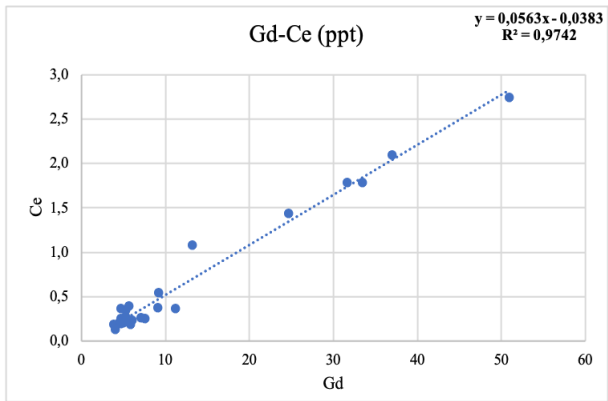
**Figure 3**



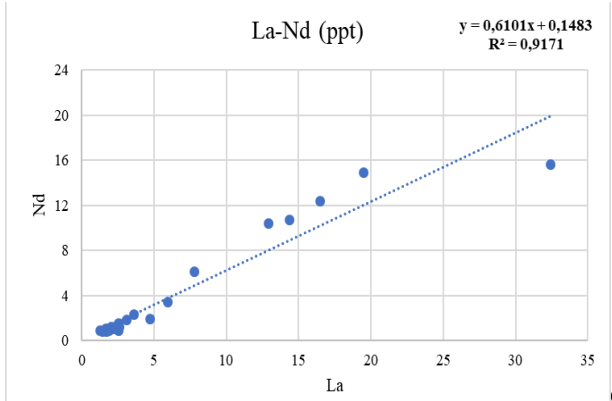
a)



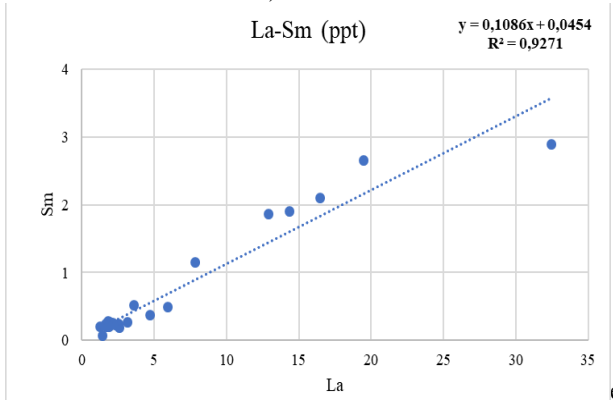
b)



c)



d)



e)

Figure 4

