From land to glass: An integrated approach for quality and traceability assessment of top Italian wines

Marcelo Enrique Conti [a], Mattia Rapa [a,*], Cristina Simone [a], Mario Calabrese [a], Gerardo Bosco [a], Silvia Canepari [b], Maria Luisa Astolfi [c,d]

[a] *Department of Management, Sapienza University of Rome, Via del Castro Laurenziano 9, 00161, Rome, Italy*
[b] *Department of Environmental Biology, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome, Italy*
[c] *Department of Chemistry, Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome, Italy*
[d] *Research Center for Applied Sciences to the Safeguard of Environment and Cultural Heritage (CIABC), Sapienza University of Rome, P.le Aldo Moro 5, 00185, Rome, Italy*

ARTICLE INFO

ABSTRACT

The wine sector in Italy is a significant contributor to the country's economy. Furthermore, Italy is renowned for producing some of the world's most excellent wines. For these reasons, the wine industry is susceptible to frauds, such as reporting false origin claims in labels. In this context, this paper aims to provide traceability and quality tool to recognise wines from different Italian regions, i.e. Calabria, Piemonte, Sicily and Veneto, from selected winemakers that reach the Top 10% in almost three international rankings. The multi-elemental analysis of soil and wine samples by ICP-MS and their chemometric treatments have identified Ni, Cs, Li, Ca, Ba, Pb, Rb, Sb, Fe and U as the most informative variables to reach optimal classification of samples. The analytical data have been used to develop an original managerial framework to leverage Pareto's Principle for effective brand-land management in the top wine segment.

1. Introduction

The wine sector in Italy is a significant contributor to the country's economy, with a revenue of 11.2 billion €. Italy consistently ranks as the world's largest wine producer. In recent years, annual wine production has averaged around 50 to 55 million hectoliters, accounting for approximately one-fifth of global wine production (Ohana-Levi & Netzer, 2023). The vineyard areas, over 700,00 ha, are spread across the entire country with different terroirs and microclimates, influencing the character and quality of wines and generating over 500 distinct grape varieties cultivated (Rapa et al., 2022). Thus, the wine sector in Italy, characterised by its rich history, diverse terroirs, indigenous grape varieties, and commitment to quality, makes it a prominent player in the global wine market. Italy is a major exporter of wine, with a strong presence in international markets. The United States, Germany, the United Kingdom, and Canada are among the top export destinations for Italian wines (Ohana-Levi & Netzer, 2023).

Italy is renowned for producing some of the world's most excellent wines, such as Brunello di Montalcino, Barolo, Barbera, Nero d'Avola, Montepulciano d'Abruzzo, and Primitivo. These top Italian wines showcase the country's remarkable winemaking tradition, combining centuries of expertise with a deep appreciation for quality and terroir, resulting in exceptional and remarkable drinking experiences (Mian et al., 2023).

For these reasons, the wine industry is susceptible to frauds, among which the most important is the production and sale of fraudulent wines that are labelled and presented as prestigious or high-value brands but contain inferior or entirely different wine, and the appellation fraud that occurs when a wine producer falsely claims that their wine originates from a prestigious or recognised wine region (Ionel, 2016a; 2016b).

Various procedures have been implemented to combat fraud in the wine sector, including improved labelling regulations, enhanced supply chain traceability, and several technologies to verify the authenticity and provenance of wines (Gayialis et al., 2022; Ionel, 2015, 2016c).

This paper aims to provide traceability and quality tool to recognise wines from different Italian regions, i.e. Calabria, Piemonte, Sicily and Veneto.

Geographical traceability is a fundamental aspect of the wine industry, ensuring consumers that the wine they purchase is authentic and from a specific region. One approach to establishing geographical

traceability is through multi-elemental analysis of soil and wine samples. This technique relies on the "terroir" which encompasses the unique characteristics of the environment in which the grapes are grown, including the soil, climate, and topography (Rapa et al., 2023a; Rapa et al., 2023b).

Multi-elemental analysis involves the quantification of various elements in soil and wine samples using various analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and atomic absorption spectroscopy (AAS). The elemental composition of soil and wine can vary depending on the geographical location, climate, and soil characteristics (Suhaj & Koreňovská, 2005).

Several studies have demonstrated the suitable use of multi-elemental analysis for geographical traceability in wine production. For example, a study conducted in Portugal showed that for some elements, the variation due to soil provenance was also observed in musts and wines, while Li, Mn, Sr and rare-earth elements (REE) allowed wine discrimination according to the vineyards (Catarino et al., 2018). Other authors have studied the grapes used to make Prosecco and found that The elements that could establish a reliable correspondence between the geolithological features of the vineyard soil and the chemical composition of grape berries are Sr, Ba, Ca, Mg, Al, K, Zn, B, Ni, Co (Pepi et al., 2017). An Argentinian study instead correctly classified 100% of the wines analysed from three regions using only seven parameters (K, Fe, Ca, Cr, Mg, Zn and Mn) and 92% correct classification for soils using seven variables (Ca, Cr, K, Fe, Cu, Zn and, Mg) (Azcarate et al., 2015).

Based on this knowledge, the aims of this paper are:

i. Multi-element analysis of soil and wine from selected winemakers in Italy that reached the Top 10% in almost three international rankings by ICP-MS;
ii. Construction of a traceability model based on chemometric treatments of data (Principal Component Analysis, Variable Stepwise, Decisional Trees, Linear Discriminant Analysis, Quadratic Discriminant Analysis, Random Forest, Naïve Bayes, Support Vector Machine, Artificial Neural Network);
iii. Provide a managerial tool converting analytical data into powerful information for stakeholders (producers, retailers, buyers, sommeliers etc.).

Notably, this paper involves the study of high-quality selected winemakers in Italy, reaching the Top 10% in almost three international rankings. In this context, it is important to provide a managerial tool to top wine producers.

Indeed, top wine management is a multifaceted field that demands a comprehensive understanding and expertise in various areas (Reynolds, 2010). Decision-makers in the wine industry must have a solid grasp of the specific land features (climate, soil chemical composition, cultural heritage, and so on), technical and business aspects of the industry and be able to harmoniously integrate the three in order to create value (Zhai et al., 2020). The selection of grapes is a critical task that requires knowledge of various grape varieties, their characteristics, and an evaluation of climatic and soil conditions. The production processes, including vinification and storage, significantly affect the quality and sensory characteristics of the wine. Distributing high-end wines can be complicated due to regulatory limitations and restrictions. Choosing distribution channels and partners is crucial for ensuring optimal market exposure and visibility (Mattiacci et al., 2019). Thoughtful planning is necessary for promoting and selling high-end wines, particularly concerning pricing and brand image. In particular, in the top wine segment is becoming more and more crucial the capability to leverage the relationship between the brand and the land: the so-called brand-land management (Atkin et al., 2017; Beckmann & Zenker, 2012; Cristófol et al., 2021; Famularo et al., 2010).

Since the end of World War II and its acceleration since the 90s, globalisation has posed increasing challenges to the top wine producers of the Old World, such as Italian, French and Spanish (The Palgrave Handbook of Wine Industry Economics, 2019). Under fierce global competition, the capability to effectively manage the brand-land relationship throughout the value chain configures a potential source of competitive advantage in the *experience goods* - i.e. products that the customers can evaluate only after the purchase (Cristófol et al., 2021; Rubini et al., 2013) - such as wine.

2. Material and methods

2.1. Reagents and materials

All reagents used were of analytical grade. For preparing standards and sample dilution and/or extraction, deionised water was used (resistivity of 18.2 MΩ cm) obtained by an Arioso (Human Corporation, Seoul, Korea) Power I RO-UP Scholar UV deioniser system. Ammonium acetate (Merck, Darmstadt, Germany) was used for soil extraction. Nitric acid super-pure grade (67%, Carlo Erba Reagents, Milan, Italy) was used for wine digestion, dilutions, and standard solution preparation. Multi-element certificate standard solution was from VWR International (Milan, Italy). Tuning solution containing 0.005 mg L^{-1} each of Ba, Be, Ce, Co, In, Pb, Mg, Tl, and Th (10.00 ± 0.05 mg L^{-1}; Spectro Pure, Ricca Chemical Company, Arlington, TX, USA), was used for inductively coupled plasma mass spectrometry (ICP-MS) instrument optimisation in order to achieve the signal/background ratio for ^{9}Be > 25,000 cps, ^{115}In >250,000 cps, ^{232}Th > 100,000 cps, CeO$^+$/Ce$^+$ <2% and Ba^{++}/Ba$^+$ <3%. Y (at 0.005 mg L^{-1} from 1000 ± 2 mg L^{-1}, Panreac Química, Barcelona, Spain), In, Rh, Sc, and Th (at 0.010 mg L^{-1} from 1000 ± 5 mg L^{-1}, Merck KGaA, Darmstadt, Germany) were used as internal standards for possible instrumental drifts and matrix effects corrections (Astolfi et al., 2020, 2021).

Table 1
Geographic coordinates of soil and wine samples collected.

Site	Latitude	Longitude
Calabria 1	39°22′76″N	17°07′01″E
Calabria 2	39°21′19″N	16°58′01″E
Calabria 3	39°33′04″N	17°06′47″E
Calabria 4	39°22′38″N	17°07′26″E
Calabria 5	39°21′18″N	16°27′12″E
Calabria 6	39°20′56″N	16°48′51″E
Piemonte 1	44°40′31″N	7°56′39″E
Piemonte 2	44°36′59″N	7°56′54″E
Piemonte 3	44°36′26″N	7°56′19″E
Piemonte 4	44°36′15″N	7°57′27″E
Piemonte 5	44°36′18″N	7°57′47″E
Piemonte 6	44°33′18″N	7°55′48″E
Piemonte 7	44°33′09″N	7°55′59″E
Piemonte 8	44°33′03″N	7°56′52″E
Piemonte 9	44°33′29″N	7°57′33″E
Piemonte 10	44°31′24″N	7°57′00″E
Sicily 1	37°41′55″N	13°05′35″E
Sicily 2	37°41′36″N	13°05′37″E
Sicily 3	37°37′54″N	13°03′17″E
Sicily 4	37°37′50″N	13°03′22″E
Sicily 5	37°37′53″N	3°03′23″E
Sicily 6	37°37′58″N	13°03′22″E
Sicily 7	37°38′52″N	13°05 ′33″E
Sicily 8	37°38′39″N	13°05 ′40″E
Sicily 9	37°38′20″N	13°05 ′12″E
Sicily 10	37°38′46″N	13°05 ′34″E
Sicily 11	37°39′00″N	13°05 ′59″E
Veneto 1	45°32′19″N	10°51′25″E
Veneto 2	45°30′51″N	10°55′07″E
Veneto 3	45°30′50″N	11°08′31″E
Veneto 4	45°30′38″N	11°08′02″E
Veneto 5	45°30′28″N	11°08′02″E

2.2. Wine and soil samples

Fifty wine samples and 32 soils (Table 1) were collected from high-quality selected winemakers in Italy, reaching the Top 10% in almost three international rankings. The grape varieties were: Gaglioppo (n = 4), Greco (n = 2), Merlot (n = 1), Cabernet (n = 1) and Chardonnay (n = 1) from the Calabria region; Barolo (n = 5), Barbera (n = 1), Nebbiolo (n = 2), Dolcetto (n = 2) from Piemonte; Corvina (n = 10) and Corvinone (n = 10) from Veneto; Sirah (n = 6) Nero D'Avola (n = 5) from Sicily. For each wine sample, soil samples were collected at regular intervals at a depth of 30 cm and 50 cm of distance from the vines. Each sample was collected in triplicate.

2.3. Sample preparation and analysis

2.3.1. Wine samples

Wine digestion was carried out in the 10 mL polypropylene tubes (Artiglass, Due Carrare, PD, Italy), adding 1 mL of each wine and 0.4 mL of 67% HNO_3; then, the tubes were placed in a water bath (WB12; Argo Lab, Modena, Italy) at 70 °C until the samples became colourless (Pérez-Álvarez et al., 2019). Once the digestion step had been completed, the samples were filled with deionised water up to 10 mL and filtered using syringe filters (0.45-μm pore size; Merck, Darmstadt, Germany). With the lack of suitable certified reference materials, spiked samples were used to evaluate the accuracy and precision of the analytical methods. The percentage recoveries (R%) for all elements were between 84 (Cr) and 120% (Se) of the expected value (Table S1). It was not possible to evaluate the R% of K due to its high concentration in the wine sample. The precision as repeatability was between 0.3 (Ga) and −20% (Cr) (Table S1).

2.3.2. Soil samples

For the leaching tests, weighed amounts (~0.5 g) of the soil samples were transferred into polypropylene tubes and then brought to a volume of 10 mL with a 1.0 M solution of CH_3COONH_4. The tubes were then covered with a cap and left under mechanical stirring for 24 h by a rotary shaker (SB2, Cheimika, SA, Italy) at room temperature (21 °C) (Gaeta, Aldega, Astolfi, Bonechi, Marra, et al., 2022; Gaeta, Aldega, Astolfi, Bonechi, Pacheco, et al., 2022). The extracted solutions were filtered with syringe filters and acidified with 100 μL of HNO_3. All samples were analysed in duplicate.

2.4. ICP-MS analysis

Multi-element determination was performed on a Bruker (Bremen, Germany) 820-MS quadrupole ICP-MS spectrometer equipped with a collision-reaction interface (CRI) and a MicroMistTM (Analytik Jena AG, Jena, Germany) nebuliser (0.4 mL/min). The CRI was in "no-gas mode" for all elements except S analysed with H_2 (100 mL/min) as skimmer gas source and As, Ca, Cr, Fe, Mn, Se, and V with He (30 mL/min) as sampler gas source and H_2 (70 mL/min) as skimmer gas source. All ICP-MS gases were 99.9995% purity and purchased from SOL Spa (Monza, Italy). Analyses were optimised at 1400 W forward power and 1.8 L/min carrier gas flow. Lens parameters were optimised for the highest signal and optimum peak shape while maintaining oxides and doubly charged ions low (Astolfi et al., 2020, 2021). The selected masses are shown in Table 2. The external calibration was prepared from multi-element standards diluted in 2% HNO_3 for wine or in 1.0 M solution of CH_3COONH_4 acidified with HNO_3 for soil samples, respectively, to obtain eight different concentration solutions (Table 2). Ten blank solutions, comprising deionised water and the reagents, were also tested with each sample set to trace and control the contributions from possible sample contamination. The blanks were deducted from all the measurements. The limits of detection (LOD) and quantification (LOQ) of the elements analysed are shown in Table 2.

Table 2
Isotope, linearity range, LOD and LOQ of wine and soil samples.

Element	Calibration range (ug/L)			Wine (μg/L)		Soil (mg/kg)	
				LOD	LOQ	LOD	LOQ
Ag107	0.5	–	10	0.03	0.1	0.00003	0.0001
Al27	1	–	50	90	300	0.03	0.1
As75	1	–	10	1	3	0.01	0.03
B11	275	–	1100	40	130	0.02	0.07
Ba137	1	–	20	5	20	0.1	0.4
Be9	0.1	–	10	0.005	0.02	0.00001	0.00004
Bi209	0.1	–	10	0.08	0.3	0.0002	0.0008
Ca44	5000	–	20,000	800	2700	0.2	0.6
Cd112	0.1	–	10	0.1	0.4	0.0004	0.001
Ce140	0.1	–	10	0.02	0.07	0.00002	0.00006
Co59	0.1	–	10	0.1	0.5	0.0002	0.0005
Cr52	5	–	20	10	30	0.1	0.3
Cs133	0.1	–	10	0.005	0.02	0.00001	0.00004
Cu65	0.1	–	50	7	24	0.0005	0.002
Dy163	0.1	–	10	0.02	0.05	0.00001	0.00004
Fe56	50	–	500	50	200	0.03	0.09
Ga71	0.5	–	10	0.01	0.04	0.00002	0.00006
Gd157	0.1	–	10	0.02	0.05	0.00002	0.00007
K39	5000	–	25,000	300	1000	0.2	0.5
La139	0.1	–	10	0.02	0.08	0.00001	0.00003
Li7	0.1	–	20	8	30	0.0006	0.002
Mg24	5000	–	25,000	200	700	0.01	0.04
Mn55	1	–	50	10	33	0.01	0.05
Mo98	0.1	–	10	0.1	0.3	0.0008	0.003
Na23	1000	–	10,000	60	180	1	4
Nb93	0.1	–	10	0.06	0.2	0.00001	0.00003
Nd146	0.5	–	10	0.04	0.1	0.00005	0.0002
Ni60	0.1	–	20	5	20	0.0004	0.001
P31	500	–	1000	200	650	0.06	0.2
Pb208	0.1	–	10	0.1	0.3	0.0003	0.0009
Pr141	0.1	–	10	0.02	0.05	0.00001	0.00004
Rb85	–	–	50	0.1	0.4	0.001	0.004
Sb121	0.1	–	10	0.01	0.02	0.002	0.008
Se76	1	–	10	1	4	0.0002	0.0007
Si28	500	–	2500	1500	5000	1	3
Sn118	0.1	–	10	0.2	0.8	0.0002	0.0005
Sr88	55	–	550	1	4	0.004	0.01
Tb159	0.1	–	10	0.01	0.04	0.00002	0.00006
Te125	0.1	–	10	0.1	0.3	0.0003	0.001
Ti49	0.1	–	10	1	2	0.0003	0.001
Tl205	0.1	–	10	0.01	0.02	0.00001	0.00004
U238	0.1	–	10	0.03	0.1	0.00001	0.00003
V51	2	–	10	9	30	0.04	0.1
W182	0.1	–	10	0.01	0.04	0.0002	0.0007
Zn66	20	–	100	10	40	0.004	0.01
Zr90	0.1	–	10	0.2	0.6	0.000004	0.00001

2.5. Statistical analysis

All descriptive statistics values were calculated for each matrix using Microsoft Excel. The obtained values below the LOD were designated as half the LOD. Analysis of variance (ANOVA) and mean comparison by Tukey's honest significant difference (HSD) for the unequal number of samples at the 5% level were performed using JMP 16.2 Pro (SAS Institute, Cary, NC, USA). Principal Component Analysis (PCA), variables stepwise, decisional trees and classification models (Linear Discriminant Analysis, Quadratic Discriminant Analysis, Naïve Bayes, Random Forest, Artificial Neural Network, Support Vector Machine) were performed with JMP 16.2 Pro. Before the chemometric assessment, an autoscaling pre-treatment was carried out on the data matrix (Rapa et al., 2023b).

3. Results and discussion

3.1. Multi-element content of the soil extractable fraction

Forty-five elements (Ag, Al, As, B, Ba, Be, Bi, Ca, Ce, Co, Cr, Cs, Cu, Dy, Fe, Ga, Gd, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Sb,

Se, Si, Sn, Sr, Tb, Te, Ti, Tl, U, V, W, Zn, Zr) were determined in soil samples from four different Italian regions (Calabria, Piemonte, Sicily and Veneto) by ICP-MS. A multi-elemental screening analysis was performed to discover specific markers for the samples' origin characterisation. The results are reported in Table 3, expressed as the mean and standard deviation for each origin region, while median, minimum and maximum values are reported in Table S2. Tukey's statistically significant difference was applied to the results, and the significant differences with a p-value <0.05 are also reported in Table 3.

At first, it is noteworthy to point out that the determination was carried out on the bio-accessible fraction of the soil and, to the best of our knowledge, this is the first time this approach was used in a traceability study. This choice was made to provide an assessment of the elements that are really accessible for the vine plants and to avoid an intense sample pre-treatment, i.e. digestion.

As notable in Table 3, it is possible to highlight specific patterns of different soil samples according to the region's origin. The soil samples from Calabria regions presented the highest content of As, B, Mn and Mo, while those from Piemonte showed the highest content of Cu and Ni. A more distinctive pattern was found for the Sicily and Veneto samples. The Sicily soil samples present the highest Ca, Co, K, Na and Rb content and the lowest Cd content. Besides, Veneto soil samples have the highest content of Ag, Be, Cd, Ce, Dy, Gd, La, Nd, P, Pb and Tb, and the lowest content of Li and Sr.

Due to the pre-treatment used, it is not possible to compare our numerical results with those reported in the literature. Nevertheless, some evaluations can be inferred.

At first it can be highlighted that we have found significant differences in twenty-four elements (above mentioned). A similar study in China found differences in ten elements, seven overlapping our results (Na, K, Mn, Rb, Sr, Li and Cd) (Hao et al., 2021).

The high concentration of Ca and K in Sicilian soil should be related to the extensive richness in primary minerals of these soils, as reported in a paper dealing with different regions of the USA (Richardson & Chase, 2021).

The same study has reported that the highest content in Cd and Pb can be related to the proximity of pollution sources of the agricultural area (Richardson & Chase, 2021). In this context, the Veneto soil, presenting the highest content of these elements, is probably closer to a pollution source.

Cu is frequently employed as a means of combatting fungal diseases and as a spray to cover the entire plant (Kelepertzis et al., 2018).

Table 3

Element contents (mg kg^{-1}, dry weight) in the soil leachable samples from different regions. Lines not connected by the same letters are statistically different.

Element	Calabria		Piemonte		Sicily		Veneto	
	mean	SD	mean	SD	mean	SD	mean	SD
Ag107	0.00008[b]	0.00004	0.00026[b]	0.00017	0.00014[b]	0.00030	0.00052[a]	0.00029
Al27	0.04	0.02	< LOD	–	< LOD	–	0.07	0.05
As75	0.16[a]	0.10	0.09[b]	0.06	0.07[b]	0.02	0.05[b]	0.06
B11	1.01[a]	0.59	0.38[b,c]	0.20	0.48[b]	0.14	0.18[c]	0.06
Ba137	6.2[b]	3.9	8.7[b]	4.0	15.0[a]	6.5	11.6[a,b]	4.7
Be9	0.00007[b]	0.00003	0.00010[b]	0.00006	0.00009[b]	0.00003	0.00022[a]	0.00007
Bi209	< LOD	–	< LOD	–	< LOD	–	< LOD	–
Ca44	8971[b]	1918	9161[b]	1116	15536[a]	2500	6430[c]	755
Cd112	0.0140[b]	0.0087	0.0186[b]	0.0090	0.0060[c]	0.0027	0.0362[a]	0.0114
Ce140	0.0158[b]	0.0050	0.0148[b]	0.0089	0.0158[b]	0.0092	0.0340[a]	0.0229
Co59	0.0997[b]	0.0655	0.0884[b]	0.0363	0.0371[a]	0.0140	0.0815[b]	0.0461
Cr52	< LOD	–	< LOD	–	< LOD	–	< LOD	–
Cs133	0.019	0.011	0.025	0.019	0.035	0.011	0.031	0.030
Cu65	0.69[b]	0.31	4.23[a]	2.64	0.17[b]	0.05	1.59[b]	1.62
Dy163	0.0016[b]	0.0004	0.0020[b]	0.0010	0.0020[b]	0.0012	0.0072[a]	0.0062
Fe56	0.17	0.12	0.26	0.23	0.15	0.24	0.13	0.08
Ga71	0.0005[b]	0.0003	0.0011[a]	0.0010	0.0002[b]	0.0001	0.0006[a,b]	0.0003
Gd157	0.0034[b]	0.0009	0.0034[b]	0.0018	0.0042[b]	0.0029	0.0141[a]	0.0130
K39	344[b,c]	57	278[c]	112	533[a]	71	406[b]	227
La139	0.0092[b]	0.0032	0.0091[b]	0.0064	0.0117[b]	0.0090	0.0527[a]	0.0530
Li7	0.179[a,b]	0.114	0.151[b]	0.060	0.218[a]	0.062	0.063[c]	0.025
Mg24	338[a,a]	139	233[b]	86	387[a]	158	212[b]	66
Mn55	68.3[a]	69.8	34.5[b]	18.8	7.5[c]	3.4	25.8[b,c]	22.2
Mo98	0.0831[a]	0.0865	0.0430[b]	0.0250	0.0165[b]	0.0067	0.0158[b]	0.0072
Na23	31[b]	28	10[b]	3	69[a]	33	11[b]	5
Nb93	< LOD	–	0.00004	0.00006	0.00005	0.00007	< LOD	–
Nd146	0.0102[b]	0.0033	0.0092[b]	0.0069	0.0122[b]	0.0095	0.0419[a]	0.0399
Ni60	0.335[b]	0.189	0.439[a]	0.095	0.214[c]	0.035	0.195[c]	0.030
P31	12.8[a]	8.5	10.1[a]	7.5	3.4[b]	2.0	8.8[a,b]	7.6
Pb208	0.0019[c]	0.0020	0.0095[b]	0.0050	0.0062[b,c]	0.0056	0.0175[a]	0.0148
Pr141	0.00175[b]	0.00059	0.00163[b]	0.00114	0.00218[b]	0.00179	0.00764[a]	0.00750
Rb85	0.41[b]	0.20	0.46[b]	0.29	1.05[a]	0.20	0.63[b]	0.27
Sb121	0.005[a,b]	0.003	0.006[a,b]	0.002	0.004[b]	0.001	0.007[a]	0.006
Se76	0.0342	0.0100	0.0337	0.0169	0.0296	0.0112	0.0299	0.0097
Si28	46[a,b]	8	40[b]	10	53[a]	11	43[a,b]	10
Sn118	< LOD	–	< LOD	–	< LOD	–	< LOD	–
Sr88	49.5[a]	21.3	34.1[b]	9.8	43.5[a,b]	12.6	10.5[c]	2.1
Tb159	0.00031[b]	0.00008	0.00035[b]	0.00017	0.00042[b]	0.00030	0.00134[a]	0.00122
Te125	< LOD	–	< LOD	–	< LOD	–	< LOD	–
Ti49	0.0030	0.0008	0.0032	0.0010	0.0073	0.0119	0.0021	0.0006
Tl205	0.0024[b]	0.0011	0.0029[a,b]	0.0011	0.0036[a,b]	0.0009	0.0041[a]	0.0030
U238	0.076[a]	0.041	0.079[a]	0.031	0.049[b]	0.014	0.041[b]	0.028
V51	< LOD	–	< LOD	–	< LOD	–	< LOD	–
W182	< LOD	–	< LOD	–	< LOD	–	< LOD	–
Zn66	0.192[a,b]	0.135	0.450[a]	0.652	0.036[b]	0.032	0.282[a,b]	0.146
Zr90	0.006[b]	0.001	0.005[b]	0.001	0.009[a]	0.003	0.011[a]	0.006

Therefore, its highest concentration in Piemonte soil can be related to a specific soil management technique.

The data treatment has highlighted some specific patterns according to geographical origin. A Principal Component Analysis (PCA) was then performed to highlight the natural grouping of samples. Five outliers (three from the Veneto region, one from Sicily and one from Calabria) have been identified by the T^2 (Mahalanobis distance), quantiles range, and Cauchy's distribution methods and were removed from the data-set. The scores and loadings plot of the unsupervised PCA are reported in Fig. 1.

The first two PCs explained 40.4% of the total variance; some evidence can be pointed out. The Veneto soil samples are all located in the upper of the scores plot and well separated from the others on PC2. The variables influencing this separation are Be, La, Ce, and Cd, previously reported by HSD discussion for Sicily samples. In addition, also the Sicily samples appeared grouped by themselves in the right-down part of the scores plot, while Piemonte and Calabria ones are partially overlapped.

Nevertheless, PCA is an unsupervised data treatment, we found a partial grouping of soil samples. These results highlight a natural differentiation of samples according to geographical origins, proving the efficiency of this approach for geographical recognition.

3.2. Multi-element wine content

The same set of forty-five elements determined in soil samples was measured in the respective wine samples from the four Italian regions (Table 4 and S3). The comparison of the element mean concentrations in the wine samples is reported in Table 4.

Some elements can be considered as geographical origin markers being statistically different for each region, i.e. B, Li and Sr. Furthermore, a similar trend was also reported in soil samples (Table 3). These elements used together can recognise the region provenience and can be employed as robust geographical origin markers. In addition, their content is high in the southern regions (Calabria and Sicily) and low in the northern ones (Piemonte and Veneto). So, it can be assumed the use of B, Li and Sr to recognise maco-region origins. Boron content is related to the vine physiology, and its deficiencies during flowering, growth and ripening of berries could cause quali-quantitative adverse effects on grapes and wine (Yermiyahu et al., 2006). Lithium is a soil-related element, but recent studies have demonstrated its abundance can improve winery grapes' nutraceutical properties, increasing phenolic compound content (Zhao et al., 2021). Strontium is usually used as a

geographical marker, and our findings agree with existing literature (Almeida & Vasconcelos, 2001; Epova et al., 2019; Lancellotti et al., 2021).

In addition to B, Li and Sr, specific patterns for wine samples from each region can be highlighted.

Calabria wine samples showed the highest content of Ga, Mo and Zn. Notably, Mo was found in the highest content in the Calabria soil samples. The Mo richness is a quality marker because its grapevine deficiency has been proposed as the primary cause of a bunch development disorder (Kaiser et al., 2005).

Piemonte samples revealed the highest content of Ag, Cu and Rb and the lowest content of P. Copper content was found in the highest concentrations in wine and soil samples from Piemonte. The Cu content in Piemonte samples is 3-fold higher than Calabria, 5-fold higher than Sicily, and 7-fold higher than Veneto. In addition, two Piemonte samples were found over the regulation limit (1 mg L^{-1}) (European Commission, 2018). These results can affect the quality of the analysed wine since Copper is widely recognised as toxic metal in elevated concentrations for plants and humans too (Ercal et al., 2001). The highest Cu content in wine samples should be related to its accumulation in grapes from soil, but there is no evidence at our disposal to relate this content to soil composition or other agricultural practices.

Besides, Sicily and Veneto wine samples also presented specific patterns of elemental concentrations. Specifically, Sicily wine samples have the highest content of Al, Ba, Be, Ce, Se, Si, Ti, Tl and Zr, while Veneto wine samples have the highest content of Cs and Mg and the lowest content of Al, K, Rb and Si.

Therefore, in this case, considering that each region showed a specific elemental pattern, a PCA was conducted to point out the natural grouping of samples.

Five outliers (four from the Sicily region and one from Calabria) have been identified by the T^2 (Mahalanobis distance), quantiles range, and Cauchy's distribution methods and were removed from the data-set. The scores and loadings plot of the unsupervised PCA was reported in Fig. 2.

The first two PCs explained the 36.3% of the total variance, and a spontaneous grouping of samples according to geographical origin can be noted. Sicily samples are located in the bottom-right quadrant of the scores plot, the Veneto ones in the bottom-left quadrant and the Piemonte ones in the upper-left quadrant. Only the Calabria samples appeared more diffused in the scores plot, however, with no overlapping with other samples.

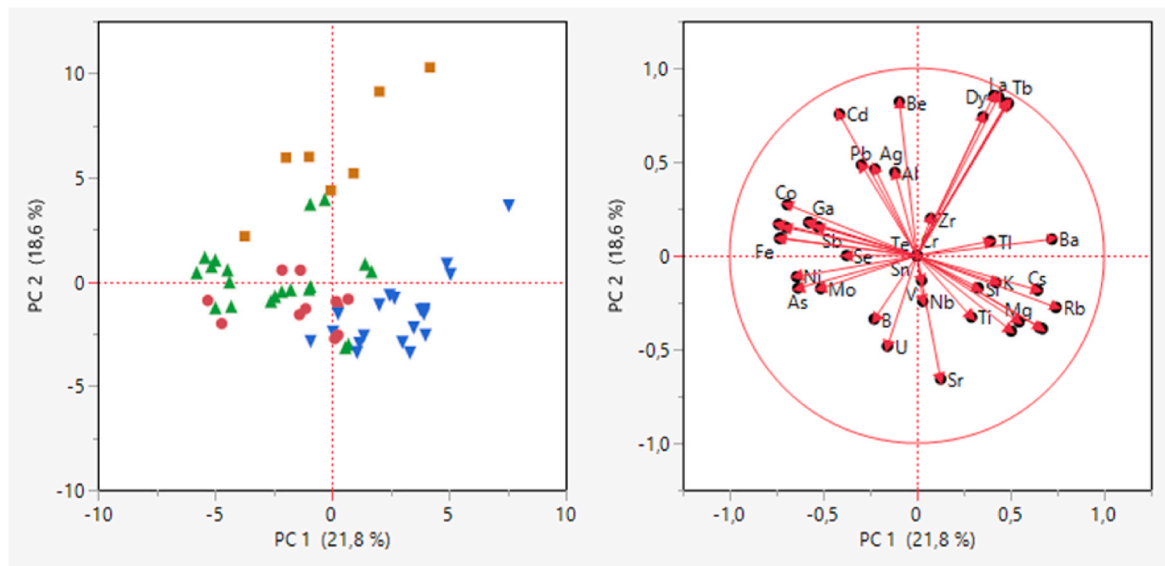The evidence found in the multivariate explorative analysis of data

Fig. 1. Scores and loading plots from PCA on soil sample results from Calabria (red), Piemonte (green), Veneto (orange) and Sicily (blue).

Table 4
Element contents (μg L^{-1}) in the wine samples from different regions. Lines not connected by the same letters are statistically different.

Element	Calabria		Piemonte		Sicily		Veneto	
	mean	SD	mean	SD	mean	SD	Mean	SD
Ag107	0.06[b]	0.04	0.17[a]	0.08	0.06[b]	0.10	0.05[b]	0.04
Al27	262[b]	118	262[b]	97	594[a]	123	98[c]	15
As75	< LOD[a,b]	–	< LOD[a,b]	–	2[a]	1	< LOD[b]	–
B11	7870[b]	2700	5780[c]	1100	9510[a]	724	3530[d]	800
Ba137	46[b]	28	36[b]	17	109[a]	26	46[b]	30
Be9	0.101[b]	0.020	0.072[b]	0.047	0.371[a]	0.187	0.025[b]	0.020
Bi209	< LOD[a,b]	–	0.12[a]	0.10	< LOD[b]	–	< LOD[a,b]	–
Ca44	88700[a]	26,000	88400[a]	12,000	64200[b]	9810	69000[b]	9800
Cd112	0.2	0.1	0.6	1.4	< LOD	–	< LOD	–
Ce140	0.23[b]	0.22	0.17[b]	0.14	0.84[a]	1.30	0.03[b]	0.01
Co59	4.0[a]	5.0	2.6[a,b]	0.4	3.8[a,b]	1.5	1.6[b]	1.0
Cr52	34[a]	25	21[b]	9	25[a,b]	9	14[b]	7
Cs133	1.81[c]	0.95	3.53[b]	0.87	3.08[b,c]	1.27	4.90[a]	2.52
Cu65	161[b]	124	496[a]	310	93[b]	87	71[b]	57
Dy163	0.04[a,b]	0.04	0.03[b]	0.01	0.09[a]	0.13	0.02[b]	0.00
Fe56	2210	1690	2280	480	2990	1300	4310	16,000
Ga71	0.64[a]	0.13	0.37[b]	0.08	0.46[b]	0.06	0.44[b]	0.25
Gd157	0.04[a,b]	0.04	0.03[a,b]	0.02	0.10[a]	0.16	< LOD[b]	–
K39	1070000[a]	360,000	1090000[a]	110,000	1090000[a]	150,000	564000[b]	290,000
La139	0.14[a,b]	0.15	0.12[b]	0.13	0.45[a]	0.75	< LOD[b]	–
Li7	48.7[a]	21.9	19.3[c]	6.3	35.7[b]	15.4	< LOD[d]	–
Mg24	118000[b]	15,000	92500[c]	8800	140000[b,c]	16,000	109000[a]	40,000
Mn55	1090[a]	320	701[b]	110	888[a,b]	320	706[b]	270
Mo98	7.6[a]	7.3	3.1[b]	1.2	2.2[b]	0.6	1.6[b]	0.8
Na23	14600[a]	4800	6540[b]	2100	16300[b]	7600	3940[a]	1600
Nb93	0.12	0.14	0.07	0.01	< LOD	–	0.15	0.33
Nd146	0.13[a,b]	0.11	0.07[b]	0.04	0.41[a]	0.71	< LOD[b]	–
Ni60	32[a]	19	34[a]	7	15[b]	4	9[b]	4
P31	254000[a]	70,000	103000[b]	16,000	205000[a]	22,000	229000[a]	140,000
Pb208	10.3[a]	10.6	2.9[b]	0.9	7.2	5.0[a,b]	2.9[b]	1.9
Pr141	0.03[a,b]	0.02	< LOD[b]	–	0.09[a]	0.15	<LOD[b]	–
Rb85	799[b]	350	1480[a]	280	816[b]	270	559[c]	180
Sb121	0.54[a]	0.20	0.23[b]	0.07	0.17[b]	0.08	0.43[a]	0.25
Se76	3[b,c]	1	3[b]	2	5[a]	2	2[c]	1
Si28	13800[b]	2900	10500[c]	1800	18900[a]	1890	9700[c]	3600
Sn118	0.9[a]	0.9	0.5[a,b]	0.4	< LOD[b]	–	< LOD[b]	–
Sr88	1260[b]	640	816[c]	340	1710[a]	380	258[d]	130
Tb159	0.02[a,b]	0.01	< LOD[b]	–	0.02[a]	0.02	< LOD[b]	–
Te125	< LOD	–	< LOD	–	< LOD	–	< LOD	–
Ti49	6[b]	1	5[b]	1	10[a]	3	6[b]	2
Tl205	0.09[b]	0.04	0.11[b]	0.07	0.23[a]	0.09	0.09[b]	0.05
U238	0.22[a,b]	0.18	0.05[b]	0.05	0.30[a]	0.32	0.12[b]	0.13
V51	< LOD	–	< LOD	–	< LOD	–	< LOD	–
W182	0.05[b]	0.06	0.12[a,b]	0.05	0.08[a,b]	0.05	0.13[a]	0.15
Zn66	989[a]	600	334[c]	200	642[b]	110	453[b,c]	260
Zr90	0.6[b]	0.5	< LOD[b]	–	2.4[a]	1.6	0.5[b]	0.7

(PCA) suggests the possible success of recognition model construction for geographical origin verification.

3.3. Classification of soil-wine system according to geographic origins

The explorative data analysis of forty-five elements content in soil and wine showed a natural grouping of samples according to geographical origin (Calabria, Piemonte, Sicilia and Veneto). Therefore, a possible classification of samples according to geographic origin should occur, according to existent literature (Han et al., 2023; Pepi et al., 2017). Specific patterns for each matrix have been highlighted, but no correlation between soil and wine was found (except for Mo from Calabria and Cu from Piemonte samples). For this reason, the two data-set composed of soil and wine results have been merged, and the new data set has undergone multivariate analysis to build classification models for geographic recognition.

At first, a variable selection was necessary to select the most informative variables for geographical recognition. Two methods of variable selection have been applied: stepwise and decisional trees. The results of the selection processes are reported in Table S4 for stepwise and Table S5 for decisional trees.

To establish a robust selection process, variables are selected by both methods. Only ten variables have been included from the forty-five elements analysed, i.e., Ni, Cs, Li, Ca, Ba, Pb, Rb, Sb, Fe and U, and they have been used in the subsequent steps. The variables chosen partially agree with a literature study that indicated, among the others, that Ba, Ca, Fe and Sb discriminate Italian soil and wine samples (Pepi & Vaccaro, 2018). In this connection, it should be noted that some of the elements we have identified (such as Ni, Cs and U) have not been studied in the above-mentioned paper.

Discriminant methods and machine learning ones have been applied to build a geographic recognition model based on wine and soil elements analyses, i.e., Linear Discriminant Analysis (LDA), Quadratic Discriminant Analysis (QDA), Random Forest (RF), Naïve Bayes (NB), Support Vector Machine (SMV), Artificial Neural Network (ANN). Table 5 reports the correct classification rates of soil-wine samples according to varieties with the six methods used.

The results appeared heterogeneous, and each classification method had different performances for the same region, probably due to the inter-class diversity of samples (Hidalgo et al., 2016). Figures of merit of the classification results are reported in Table S6. The error rates range from 27.5 % to 37.5 % for all the classification methods involved
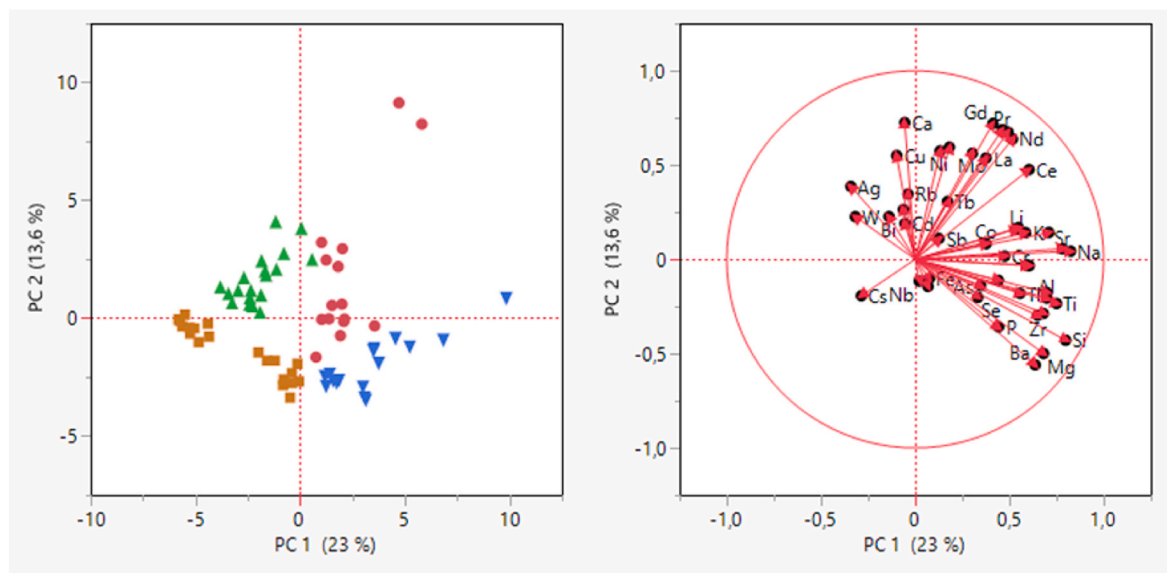
Fig. 2. Scores and loading plots from PCA on wine sample results Calabria (red), Piemonte (green), Veneto (orange) and Sicily (blue).

Table 5
Percentage of samples correct classification for geographical origin in training, validation and test steps.

		CALABRIA	PIEMONTE	SICILY	VENETO
LDA	*Training*	81.8%	100%	66.7 %	81.8%
	Validation	30.5%	93.8%	66.7%	60%
	Test	60%	75%	75%	66.7%
	Mean	**57.4%**	**89.6%**	**69.5%**	**69.5%**
QDA	*Training*	81.8%	93.8%	73.3%	81.8%
	Validation	0%	93.8%	46.7%	70%
	Test	60%	100%	50%	33%
	Mean	**47.3%**	**95.9%**	**56.7%**	**61.6%**
RF.	*Training*	81.8%	100%	100%	90.9%
	Validation	27.3%	87.5%	100%	70%
	Test	40%	87.5%	100%	50%
	Mean	**49.7%**	**91.7%**	**100 %**	**70.3%**
NB	*Training*	81.8%	100%	46.7%	81.8%
	Validation	36.4%	81.3%	31.3%	50%
	Test	60%	75%	37.5%	66.7%
	Mean	**59.4%**	**85.4%**	**38.5%**	**66.2%**
SVM	*Training*	81.8%	100%	53.3%	81.8%
	Validation	30%	100%	40%	60%
	Test	60%	87.5%	37.5%	66.7%
	Mean	**57.3%**	**95.8%**	**43.6%**	**69.5%**
ANN	*Training*	81.8%	93.8%	100%	81.8%
	Validation	30%	87.5%	80%	60%
	Test	60%	75%	87.5%	50%
	Mean	**57.3%**	**85.4%**	**89.2%**	**63.9%**

(Table S6). Therefore, the integrated use of six classification methods allows finding the best classifier for each group of samples.

Samples from the Piemonte region were well classified with all the methods involved, with a minimum of 85.4% of correct classification with ANN and NB and 95.9% of correct classification with QDA.

Sicily samples reached the best classification with ANN (89.2%) and RF (100%), while with the other methods, the correct classification ranged from 38.5% to 69.5%.

A partial correct classification was achieved for Veneto regions, indeed, the samples correctly classified varied from 61.6% of QDA to 70.3% of RF. The Calabria region appeared as the less recognizable region with the analyses performed, attesting a correct classification for 59.4% with NB. On the other hand, the Calabria samples showed a specific pattern of Mo content in the wine-soil system. So, their integrated assessment might be suitable for the recognition of this region.

The incorrect classification can be attributed to the confusing attribution in the northern (Piemonte and Veneto) and southern regions (Calabria and Sicily). Several Calabria samples have been identified as Sicilian, and many Veneto samples as Piemonte. This finding leads to a satisfactory classification of wine-soil samples according to macro-region provenience.

Furthermore, our results are in good agreement with the only other study that merges soil and wine data before performing chemometrics. Indeed, Pepi & Vaccaro, 2018 reached 84.82% of correct classification of their samples but performing only LDA and analysing samples coming from a single Italian region (Pepi & Vaccaro, 2018).

Nevertheless, using different classification methods allowed the possibility to perform a useful classification of Piemonte and Sicily samples. As previously reported (Rapa et al., 2022; 2023a), QDA, ANN, and RF treatment on multi-elemental analysis resulted to be suitable tools for geographic origin recognition.

3.4. Managerial implications

With the aim to contribute to an effective, value-oriented top wine management, this section introduces an original way to utilise multi-elemental analytical data and their multivariate analysis.

Regarding the Italian top wines put under focus in this research, we found that 20% of variables explored (Ni, Cs, Li, Ca, Ba, Pb, Rb, Sb, Fe and U) in the soil-wine system based on geographical origins account for 80% of the geographical recognition. This type of relationship, that is
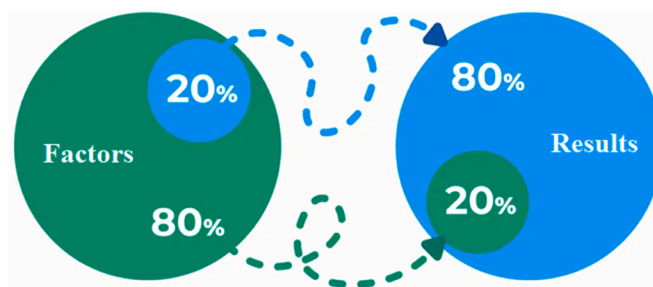

Fig. 3. The Pareto Principle: 20% of factors in the soil-wine system account for 80% of geographic recognition.

naturally occurred, is known as Pareto's principle (Fig. 3).

Vilfredo Pareto's principle, developed in 1916, posits that a minority of causes is responsible for most effects, with 80% of results stemming from just 20% of actions. This fundamental concept is widely applicable across various industries but is particularly relevant in economics and management, where it is commonly employed to identify strategic areas for maximising returns (Sanders, 1987).

Appreciating Pareto's Principle is crucial since it empowers decision-makers to determine which endeavours to prioritise for optimal effect (Craft & Leake, 2002). When a work can be decomposed into smaller units, Pareto's principle can be a valuable tool for identifying the component of the work that holds the most sway (Wyper & Harrison, 2000). Pareto's analysis and charts are indispensable tools in the realm of quality control. Applying Pareto charts for product quality control enables the effective visualisation of data, facilitating the identification of actions that require priority attention (Ali & Johl, 2022)). The primary objective of this methodology is to diminish process variations, thereby enhancing production output. Pareto charts are widely utilised in quality control due to their capacity to expeditiously pinpoint the primary sources of process variation. Incorporating the Pareto principle can substantially impact with minimal effort, improving overall efficiency and enabling targeted initiatives (Grosfeld-Nir et al., 2007). By appropriately prioritising initiatives, the 80/20 law can be a valuable tool in boosting metrics more efficiently. In doing so, the Pareto principle can effectively amplify the impact of undertaken activities while simultaneously reducing the time needed to achieve desired outcomes (Pareto, 1916).

This outcome provides valuable support in managerial decisions regarding factors to leverage for a successful brand-land strategy. In this case, using analytical data, it was possible to leverage the brand-land (soil dimension) management by the 80/20 principle of Pareto.

4. Conclusions

Italy is renowned for producing some of the world's most excellent wines, combining centuries of expertise with a deep appreciation for quality and terroir, resulting in exceptional and remarkable drinking experiences. For these reasons, the wine industry is susceptible to frauds, such as reporting false origin claims in labels. In this context, this paper aimed to provide traceability and quality tool to recognise wines from different Italian regions, i.e. Calabria, Piemonte, Sicily and Veneto, from selected winemakers that reach the Top 10% in almost three international rankings. The multi-elemental analysis of soil and wine samples by ICP-MS highlighted that B, Li and Sr could be considered geographical origin markers. These elements can be employed as robust geographical origin markers, being their content high in the Italian Southern Regions and low in the Northern ones, to recognise macro-region origins.

PCA's explorative analysis of data of forty-five elements content in soil and wine showed a natural grouping of samples according to geographical origin. Furthermore, Ni, Cs, Li, Ca, Ba, Pb, Rb, Sb, Fe and U have been selected as the most informative variables to recognise samples origin, and they have been involved in constructing classification models by LDA, QDA, RF, NB, SVM and ANN. Using different chemometrics classification methods allowed the possibility to perform a suitable classification (up to 100%) of Piemonte and Sicily samples. In addition, the analytical data have been converted into powerful information for stakeholders (producers, retailers, buyers, sommeliers etc.) by providing a managerial tool applying Pareto's Principle. In conclusion, we have developed an original framework in the present study to leverage Pareto's Principle for effective, value-oriented brand-land management in the top wine segment.

The study has some limitations due to the to the fact that samples from only four regions were analysed. The regions taken into consideration are those that have the greatest impact on the Italian wine market. Despite this, future research will be able to analyse the top

wines from all the other Italian regions to provide an even more specific and recognizable tool.

CRediT authorship contribution statement

Marcelo Enrique Conti: Conceptualization, Methodology, Validation, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Mattia Rapa:** Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Funding acquisition. **Cristina Simone:** Conceptualization, Methodology, Investigation, Resources, Writing – original draft, Writing – review & editing. **Mario Calabrese:** Methodology, Investigation, Resources, Writing – review & editing, Visualization, Project administration, Funding acquisition. **Gerardo Bosco:** Methodology, Investigation, Resources, Writing – review & editing, Visualization, Project administration. **Silvia Canepari:** Methodology, Validation, Resources, Data curation, Writing – review & editing, Visualization, Supervision. **Maria Luisa Astolfi:** Conceptualization, Methodology, Validation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodcont.2023.110226.

References

Ali, K., & Johl, S. K. (2022). Critical success factors of total quality management practices using Pareto analysis. *International Journal of Productivity and Quality Management, 36*(3). https://doi.org/10.1504/IJPQM.2022.124704

Almeida, C. M., & Vasconcelos, M. T. S. D. (2001). ICP-MS determination of strontium isotope ratio in wine in order to be used as a fingerprint of its regional origin. *Journal of Analytical Atomic Spectrometry, 16*(6). https://doi.org/10.1039/b100307k

Astolfi, M. L., Conti, M. E., Marconi, E., Massimi, L., & Canepari, S. (2020). Effectiveness of different sample treatments for the elemental characterization of bees and beehive products. *Molecules*. https://doi.org/10.3390/molecules25184263

Astolfi, M. L., Marconi, E., Vitiello, G., & Massimi, L. (2021). An optimized method for sample preparation and elemental analysis of extra-virgin olive oil by inductively coupled plasma mass spectrometry. *Food Chemistry, 360*. https://doi.org/10.1016/j.foodchem.2021.130027

Atkin, T., Wilson, D., Thach, L., & Olsen, J. (2017). Analyzing the impact of conjunctive labeling as part of a regional wine branding strategy. *Wine Economics and Policy, 6*(2). https://doi.org/10.1016/j.wep.2017.10.003

Azcarate, S. M., Martinez, L. D., Savio, M., Camiña, J. M., & Gil, R. A. (2015). Classification of monovarietal Argentinean white wines by their elemental profile. *Food Control, 57*. https://doi.org/10.1016/j.foodcont.2015.04.025

Beckmann, S. C., & Zenker, S. (2012). *Place branding: A multiple stakeholder perspective.* 41st European Marketing Academy Conference (EMAC).

Catarino, S., Madeira, M., Monteiro, F., Caldeira, I., de Sousa, R. B., & Curvelo-Garcia, A. (2018). Mineral composition through soil-wine system of Portuguese vineyards and its potential for wine traceability. *Beverages, 4*(4). https://doi.org/10.3390/beverages4040085

Craft, R. C., & Leake, C. (2002). The Pareto principle in organizational decision making. *Management Decision, 40*(8). https://doi.org/10.1108/00251740210437699

Cristófol, F. J., Cruz-Ruiz, E., & Zamarreño-Aramendia, G. (2021). Transmission of place branding values through experiential events: Wine bc case study. *Sustainability, 13* (6). https://doi.org/10.3390/su13063002

Epova, E. N., Bérail, S., Séby, F., Vacchina, V., Bareille, G., Médina, B., Sarthou, L., & Donard, O. F. X. (2019). Strontium elemental and isotopic signatures of Bordeaux wines for authenticity and geographical origin assessment. *Food Chemistry.* https://doi.org/10.1016/j.foodchem.2019.04.068

Ercal, N., Gurer-Orhan, H., & Aykin-Burns, N. (2001). Toxic metals and oxidative stress part I: Mechanisms involved in metal-induced oxidative damage. *Current Topics in Medicinal Chemistry, 1*(6). https://doi.org/10.2174/1568026013394831

European Commission. (2018). COMMISSION REGULATION (EU) 2023/915 of 25 April 2023 on maximum levels for certain contaminants in food and repealing Regulation (EC) No 1881/2006. *Official Journal of the European Union, 2016*(68).

Famularo, B., Bruwer, J., & li, E. (2010). Region of origin as choice factor: Wine knowledge and wine tourism involvement influence. *International Journal of Wine Business Research, 22*(4). https://doi.org/10.1108/17511061011092410

Gaeta, M., Aldega, L., Astolfi, M. L., Bonechi, B., Marra, F., Pacheco, P., Perinelli, C., & Tiberi, F. (2022). Soils developed on the Si-poor, alkali-rich pyroclastic rocks of the Colli Albani volcanic district (Central Italy): The effect of leucite, clinopyroxene and phlogopite on the base cations mobility. *Applied Geochemistry, 145.* https://doi.org/10.1016/j.apgeochem.2022.105430

Gaeta, M., Aldega, L., Astolfi, M. L., Bonechi, B., Pacheco, P., & Perinelli, C. (2022). Base cation mobility in vineyard soils of the colli albani volcanic district (Central Italy). *Journal of Soil Science and Plant Nutrition, 22*(4). https://doi.org/10.1007/s42729-022-01039-9

Gayialis, S. P., Kechagias, E. P., Papadopoulos, G. A., & Kanakis, E. (2022). *A smart-contract enabled blockchain traceability system against wine supply chain counterfeiting. IFIP advances in information and communication technology* (Vol. 663). IFIP. https://doi.org/10.1007/978-3-031-16407-1_56

Grosfeld-Nir, A., Ronen, B., & Kozlovsky, N. (2007). The Pareto managerial principle: When does it apply? *International Journal of Production Research, 45*(10). https://doi.org/10.1080/00207540600818203

Han, X., Lu, H. C., Wang, Y., Gao, X. T., Li, H. Q., Tian, M. B., Shi, N., Li, M. Y., Yang, X. L., He, F., Duan, C. Q., & Wang, J. (2023). Region, vintage, and grape maturity co-shaped the ionomic signatures of the Cabernet Sauvignon wines. *Food Research International, 163.* https://doi.org/10.1016/j.foodres.2022.112165

Hao, X., Gao, F., Wu, H., Song, Y., Zhang, L., Li, H., & Wang, H. (2021). From soil to grape and wine: Geographical variations in elemental profiles in different Chinese regions. *Foods, 10*(12). https://doi.org/10.3390/foods10123108

Hidalgo, M. J., Fechner, D. C., Marchevsky, E. J., & Pellerano, R. G. (2016). Determining the geographical origin of Sechium edule fruits by multielement analysis and advanced chemometric techniques. *Food Chemistry, 210.* https://doi.org/10.1016/j.foodchem.2016.04.120

Ionel, B. (2015). *Foundations of veterinary sanitary and food safety legislation (Bazele legislatiei sanitar-veterinare si pentru siguranta alimentelor)* (Vol. I).

Ionel, B. (2016a). EUROPEAN regulation in the veterinary sanitary and food safety area, a component of the EUROPEAN policies on the safety of food products and the protection of consumer interests: A 2007 retrospective. Part two: Regulations. *Revista Universul Juridic ISSN, 2393–3445,* 16–19.

Ionel, B. (2016b). EUROPEAN regulation in the veterinary sanitary and food safety area, a component of the EUROPEAN policies on the safety of food products and the protection of consumer interests: A 2007 retrospective. Part two: Regulations. *Revista Universul Juridic ISSN, 2393–3445,* 16–19.

Ionel, B. (2016c). EUROPEAN regulation in the veterinary sanitary and food safety area, component of EUROPEAN policies on the safety of food products and the protection of consumer interests: A 2007 retrospective. Part three: Directives. *Revista Universul Juridic ISSN, 2393–3445,* 21–23.

Kaiser, B. N., Gridley, K. L., Brady, J. N., Phillips, T., & Tyerman, S. D. (2005). The role of molybdenum in agricultural plant production. *Annals of Botany, 96*(5). https://doi.org/10.1093/aob/mci226

Kelepertzis, E., Botsou, F., Patinha, C., Argyraki, A., & Massas, I. (2018). Agricultural geochemistry in viticulture: An example of Cu accumulation and geochemical fractionation in Mediterranean calcareous soils (Nemea region, Greece). *Applied Geochemistry, 88.* https://doi.org/10.1016/j.apgeochem.2017.04.013

Lancellotti, L., Sighinolfi, S., Ulrici, A., Maletti, L., Durante, C., Marchetti, A., & Tassi, L. (2021). Tracing geographical origin of Lambrusco PDO wines using isotope ratios of oxygen, boron, strontium, lead and their elemental concentration. *Current Research in Food Science.* https://doi.org/10.1016/j.crfs.2021.11.001

Mattiacci, A., Bruni, A., Magno, F., & Cassia, F. (2019). Sales capabilities in the wine industry: An analysis of the current scenario and emerging trends. *British Food Journal, 121*(12). https://doi.org/10.1108/BFJ-04-2019-0231

Mian, G., Nassivera, F., Sillani, S., & Iseppi, L. (2023). Grapevine resistant cultivars: A story review and the importance on the related wine consumption inclination. *Sustainability, 15*(1). https://doi.org/10.3390/su15010390

Ohana-Levi, N., & Netzer, Y. (2023). Long-term trends of global wine market. *Agriculture, 13*(1). https://doi.org/10.3390/agriculture13010224

Pareto, V. (1916). Trattato di Sociologia generale. In *Trattato di Sociologia generale.*

Pepi, S., Sansone, L., Chicca, M., & Vaccaro, C. (2017). Relationship among geochemical elements in soil and grapes as terroir fingerprintings in Vitis vinifera L. cv. "Glera.". *Chemie der Erde, 77*(1). https://doi.org/10.1016/j.chemer.2017.01.003

Pepi, S., & Vaccaro, C. (2018). Geochemical fingerprints of "Prosecco" wine based on major and trace elements. *Environmental Geochemistry and Health, 40*(2). https://doi.org/10.1007/s10653-017-0029-0

Pérez-Álvarez, E. P., Garcia, R., Barrulas, P., Dias, C., Cabrita, M. J., & Garde-Cerdán, T. (2019). Classification of wines according to several factors by ICP-MS multi-element analysis. *Food Chemistry, 270.* https://doi.org/10.1016/j.foodchem.2018.07.087

Rapa, M., Ferrante, M., Rodushkin, I., Paulukat, C., & Conti, M. E. (2023a). Heavy metals, rare earth elements and isotopic fingerprint of Venetian Protected Designation of Origin sparkling wines. *British Food Journal, 125*(7). https://doi.org/10.1108/BFJ-06-2022-0483

Rapa, M., Ferrante, M., Rodushkin, I., Paulukat, C., & Conti, M. E. (2023b). Venetian Protected Designation of origin wines traceability: Multi-elemental, isotopes and chemometric analysis. *Food Chemistry, 404.* https://doi.org/10.1016/j.foodchem.2022.134771

Rapa, M., Giannetti, V., & Boccacci Mariani, M. (2022). Characterization of polyphenols in a Sicilian autochthonous white grape variety (PDO) for monitoring production process and shelf-life of wines. *Agriculture, 12*(11). https://doi.org/10.3390/agriculture12111888

Reynolds, A. G. (2010). Managing wine quality: Viticulture and wine quality. In *Managing wine quality: Viticulture and wine quality.* https://doi.org/10.1533/9781845699284

Richardson, J. B., & Chase, J. K. (2021). Transfer of macronutrients, micronutrients, and toxic elements from soil to grapes to white wines in uncontaminated vineyards. *International Journal of Environmental Research and Public Health, 18*(24). https://doi.org/10.3390/ijerph182413271

Rubini, L., Motta, L., & Di Tommaso, M. R. (2013). Quality-based excellence and product-country image: Case studies on Italy and China in the beverage sector. *Measuring Business Excellence, 17*(2). https://doi.org/10.1108/13683041311329429

Sanders, R. (1987). The pareto principle: Its use and abuse. *Journal of Services Marketing, 1*(2). https://doi.org/10.1108/eb024706

Suhaj, M., & Koreňovská, M. (2005). Application of elemental analysis for identification of wine origin: A review. *Acta Alimentaria, 34*(Issue 4). https://doi.org/10.1556/AAlim.34.2005.4.7

The Palgrave Handbook of Wine Industry Economics. (2019). In *The Palgrave Handbook of wine industry economics.* https://doi.org/10.1007/978-3-319-98633-3

Wyper, B., & Harrison, A. (2000). Deployment of six sigma methodology in human resource function: A case study. *Total Quality Management, 11*(4–6). https://doi.org/10.1080/09544120050008129

Yermiyahu, U., Ben-Gal, A., & Sarig, P. (2006). Boron toxicity in grapevine. *HortScience, 41*(7). https://doi.org/10.21273/hortsci.41.7.1698

Zhai, Z., Martínez, J. F., Beltran, V., & Martínez, N. L. (2020). Decision support systems for agriculture 4.0: Survey and challenges. *Computers and Electronics in Agriculture, 170.* https://doi.org/10.1016/j.compag.2020.105256

Zhao, H., Xie, X., Read, P., Loseke, B., Gamet, S., Li, W., & Xu, C. (2021). Biofortification with selenium and lithium improves nutraceutical properties of major winery grapes in the Midwestern United States. *International Journal of Food Science and Technology, 56*(2). https://doi.org/10.1111/ijfs.14726