

Article

Geological Influences on Wine Quality: Analyzing Nebbiolo Grapes from Northern Italy

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Abstract: This study investigates the critical relationship between soil characteristics, trace element concentrations in Nebbiolo grapes, and the resulting wine quality, emphasizing the importance of terroir in winemaking. Italy, particularly the regions of Piedmont, Lombardy, and the Aosta Valley, is home to Nebbiolo, a prestigious grape variety known for its depth and aging potential in wines like Barolo and Barbaresco. The research focuses on seventeen grape and wine samples, highlighting how soil mineral composition could affect grape composition and wine characteristics. The analysis employed ICP-AES (inductively coupled plasma atomic emission spectrometry) to measure trace elements such as Al, Ba, and Mn, linking their concentrations to the soil's geological properties. Elements were categorized into three groups based on their origins—natural soil contributions (Al, Ba, Li, Mn, Mo, Sr, Ti), those influenced by production cycles (Ca, Mg, K, Cu, Zn, Fe), and artificial sources (Co, Cr, Ni, V)—asserting that the first group serves as the most reliable indicators for tracing wines back to their vineyard origins. By establishing a chemical fingerprint for Nebbiolo wines, this research aims to enhance their authenticity and market value while providing insights into the intricate interplay between soil, grape varieties, and winemaking practices and contemporary challenges like climate change and evolving market demands.

Keywords: *Vitis vinifera* L.; mineral content; ICP-AES



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1. Introduction

Wine has been a quintessential product of Europe for thousands of years, particularly in the Mediterranean basin. Today, the foremost global wine producers are Italy, France, and Spain, with Italy distinguished by its vast array of indigenous grape varieties. This diversity sets Italian wines apart from those produced elsewhere, highlighting the intricate relationship between grape cultivation and regional characteristics. The quality of wine is closely linked to the quality of the grapes; optimal conditions for cultivation—healthy vines at the right level of ripeness—are essential for producing high-quality wines [1]. Consequently, exceptional wines are born in the vineyard rather than the cellar.

The characteristics of wine are profoundly influenced by grape variety and the vineyard's environmental conditions, particularly the soil's composition, which plays a crucial role in determining the final product's quality [2,3]. The qualitative and quantitative composition of the inorganic matrix of wine can accurately trace its vineyard of origin, as this is inherently linked to the soil in which the vines grow, the nutrient drainage, and the geological and geochemical properties of the vineyard substrate. Research has shown that specific soil characteristics, such as texture and mineral content, directly impact vine physiology and grape composition, ultimately influencing wine quality [4–6].

In this context, determining the concentrations of specific trace elements in grapes destined for wine production is essential. Mineral substances, cations, and anions of geological origin are absorbed through the plant's roots and incorporated into the biological tissues of the grape. The concentration of these substances, particularly the cationic fraction, often exists in parts per billion (ppb). Notable elements such as Al, Ba, Mn, Mo, Rb, Si, Sr, and Ti are particularly relevant, as their concentrations reflect the mineral contributions of the soil and the grape clusters' capacity to absorb these metals [7]. Advanced instrumentation allows for the detection of these trace elements, with their relative distribution strongly correlated with the mineralogical composition of the soils, as evidenced, for example, by Teixeira et al. [8], which reported the straight correlation between isotopic Sr and Pb composition in soils and wines. The Italian peninsula, with its complex tectonic evolution, offers a favorable environment for such studies, resulting in an extremely diverse geological and lithological landscape [7,9].

For premium wines, certification of authenticity and geographical provenance is critical for enhancing market value. Scientific methods can support the artistry of winemaking by establishing a chemical, organic, and geochemical fingerprint for the wine, facilitating effective traceability [7]. Quantifying the inorganic matrix of wine enables precise identification of its vineyard of origin, closely linked to the land's geological and geochemical characteristics [2].

This study analyzes nearly fifty samples of Nebbiolo grapes, musts, and wines sourced from various regions in Northern Italy—specifically Langhe and Canavese (Piedmont), Valtellina (Lombardy), and the small area at the beginning of the Aosta Valley. Nebbiolo is renowned as one of Italy's finest grape varieties, producing esteemed red wines such as Barolo and Barbaresco, known for their depth and aging potential [10,11]. This grape also holds significant cultural and economic importance in Piedmont, a region recognized for its high-quality agricultural production, particularly in the wine sector, which boasts 14 DOCG and 46 DOC designations, many derived from indigenous grapes [10].

Characterized by its late ripening and susceptibility to climatic variability, Nebbiolo flourishes in specific terroirs that enhance its distinctive attributes [12]. The grape's name originates from the Italian term "nebbia," meaning fog, a phenomenon prevalent in the Langhe area during harvest that significantly influences the ripening process and the phenolic composition of the grapes [13]. A defining feature of Nebbiolo wines is their remarkable acidity, robust tannins, and complex aromatic profile, often showcasing notes of cherry, rose petal, tar, and earthy undertones [14]. These characteristics are deeply intertwined with the specific soil types prevalent in its growing regions, including the calcareous marl of Barolo and the sandy soils of Barbaresco, each imparting unique mineral qualities that affect the sensory attributes of the wine [15]. Research has demonstrated that soil composition directly influences nutrient uptake and phenolic development in Nebbiolo grapes, subsequently affecting wine quality [15].

The role of soil in shaping Nebbiolo's profile extends beyond basic nutrient supply; it is instrumental in determining water retention and drainage, which are critical for the grape's late maturation [16]. Variations in soil texture can lead to different levels of water stress, directly impacting grape composition and the sensory attributes of the resulting wines [17]. Furthermore, the interaction between soil microbiota and vine health is pivotal, as certain soil microorganisms can enhance grape quality by improving nutrient availability and promoting plant vigor [18–20].

Aging potential is another critical aspect of Nebbiolo, with many wines benefiting from extended maturation in oak barrels and bottles, allowing for the integration of tannins and the emergence of complex tertiary aromas [21]. The interplay between grape phenolics, soil characteristics, and aging practices presents a rich area for exploration, providing

insights into how these factors collectively optimize the sensory attributes of Nebbiolo wines [14,15].

Despite its esteemed status, the Nebbiolo grape faces contemporary challenges, including climate change and evolving market demands. Understanding the specific characteristics of this cultivar in relation to soil and vineyard practices is essential for both producers and consumers.

The work presented here focused on evaluating the presence of metals in soil and their transfer to grapes. We also investigated the variation in the concentrations of these elements throughout different production phases, from grape juice to wine. A key aspect of our study was the development of a mineralization method for grapes, musts, and soils. For the wine, we applied acidification using nitric acid followed by dilution. We analyzed nineteen elements: Ca, K, Mg, Al, Ba, Cu, Fe, Mn, Sr, Zn, Co, Cr, Li, Mo, Ni, Sb, Ti, V, and Zr. Some of these elements are more stable and less prone to pollution, while others exhibited significant concentration variations due to the processing cycles of grapes and musts in wine production. The final distribution of the elements is thus the result of a combination of factors, some of which may be uncontrollable or discriminatory. In general, the variables can be divided into three groups based on their discriminating power [22]:

- (a) Elements whose concentration in the wine is not influenced by the production cycle, but rather by the mineral contribution of the soil and its ability to transfer elements from the soil to the berries, which is further conditioned by the characteristics of the plant. These elements include Al, Ba, Li, Mn, Mo, Si, Sr, and Ti, whose presence can be attributed to artificial sources only when illicit treatments are conducted during production.
- (b) Elements whose concentration results from both natural factors and those derived from the production cycle. Among these are the following:
 - Ca and Mg, which are natural components of the must and whose concentrations increase in the wine following the addition of carbonates to reduce acidity.
 - Cu and Zn, which can be absorbed from the soil and are derived from fungicide treatments (Bordeaux mixture, zinc dithiocarbamates) and/or from winemaking equipment.
 - Fe, which can be absorbed from the soil by *Vitis vinifera* or derived from soil particle traces but can also come from equipment or steel containers used in production phases.
 - K, the predominant cation in grape juice, which is derived from *Vitis vinifera* but also comes from the addition of metabisulfite or carbonate.
- (c) Elements that are derived almost exclusively from artificial sources are as follows:
 - Co, Cr, Ni, and V, which are present at very low concentrations and are more likely to result from the interaction of musts and wines with metal containers than from absorption from the soil.

The best candidates for correlating wines and soils are the elements in the first group, as anthropogenic intervention is extremely limited for these. However, the other elements cannot be excluded, as they can act as optimal tracers in the presence of particular soils; for instance, iron concentration can be significant in the cultivation of soils rich in pyrite.

In summary, this study presents a thorough examination of the concentrations of specific trace elements in Nebbiolo grapes, exploring their geological origins and implications for wine quality and authenticity.

2. Materials and Methods

2.1. Reagents and Standards

Nitric acid, hydrochloric acid, and hydrofluoric acid, with trace analysis grade purity, were purchased from Sigma-Aldrich (Merck group, Milan, Italy). Certified mono-element solutions with a concentration of 1000 mg/L were purchased for each element analyzed from Sigma Aldrich (Merck group, Milan, Italy); ultrapure water was obtained by a Millipore Milli-Q® Direct 8 system (Merck group, Milan, Italy) and used to prepare all the standard solutions and samples dilutions. Gradient-grade Ethanol was purchased from the Sigma-Aldrich division of Merck group (Milan, Italy).

2.2. Standard Solutions Preparation

Our study focused on 19 elements present in variable concentrations in all the matrices (soil, grapes, must, wine) under investigation: Ca, K, Mg, Al, Ba, Cu, Fe, Mn, Sr, Zn, Co, Cr, Li, Mo, Ni, Sb, Ti, V and Zr. As the range of concentrations in each matrix should be quite different, we decided to prepare multiple standards, with different elements based on their range of concentration.

The standards were prepared in 50-mL flasks with the desired dilution of each mono-element standard; in each flask, 2 mL of 65% nitric acid and 0.50 mL of absolute ethanol were added to provide the same composition of wine samples [23]. Table 1 reports the ranges of concentration for each element considered.

Table 1. Concentration range used to prepare standard solutions and calibration curves, for each element considered in current study.

Element	Concentration Range (ppm)
Ca	5–100
K	50–250
Mg	5–100
Al	0.1–1.0
Ba	0.1–1.0
Cu	0.1–1.0
Fe	5–20
Mn	0.5–5.0
Sr	0.1–1.0
Zn	0.5–5.0
Co	0.02–0.20
Cr	0.02–0.20
Li	0.02–0.20
Mo	0.1–1.0
Ni	0.1–1.0
Sb	0.1–1.0
Ti	0.02–0.20
V	0.02–0.20
Zr	0.02–0.20

Blank solutions were prepared in a 50-mL flask with 2 mL of 65% nitric acid and 0.50 mL of pure ethanol and diluted with ultrapure water.

The data processing was carried out based on the results provided by the instrument; according to the amount of the initial sample considered, it was possible to determine the actual concentrations of the metals present in each matrix (soil, grape, must, wine), expressed as [mg of element/kg of matrix].

2.3. Sample Preparation

2.3.1. Sites

The sampling sites were selected from various regions of northern Italy, chosen for their strong association with the widespread cultivation of the Nebbiolo grape variety (*Vitis vinifera* L.), well known for producing prestigious DOC (Denomination of Controlled Origin) and DOCG (Denomination of Controlled and Guaranteed Origin) red wines. Specifically, the sites chosen for sampling included Monforte (44.5829° N, 7.9679° E) and Sinio (44.5998° N, 8.0217° E) in Langhe (South Piedmont); Ghemme (45.5984° N, 8.4209° E), Gattinara (45.6172° N, 8.3709° E), and Piverone (45.4478° N, 8.0072° E) in Canavese (North Piedmont); Donnas (45.6030° N, 7.7662° E) in the Aosta Valley; and Sondrio (46.1713° N, 9.8694° E) in Valtellina (Lombardy).

2.3.2. Soil Samples

Eleven soils were chosen in the sites reported above and classified as follows: samples S1, S2, S3, and S11 came from Canavese; S4, S5, and S8 from Langhe; and S6, and S7 from Aosta Valley; S9 and S10 from Valtellina. Langhe vineyards are characterized by calcareous limestone soils (pH > 8), whereas the soils of Canavese, Valtellina, and Aosta Valley are reported to have an acidic or sub-acidic pH, with significantly lower percentages of clay [24–26].

Soil samples were collected at two depths (0–0.10 m and 0.10–0.30 m) at 1.50 m intervals parallel to the rows of vines, progressing in alternating rows. A 0.10 m diameter auger (manually operated) was used to collect the samples, and it was thoroughly cleaned between sampling sites. The soil samples were then placed into labeled polyethylene bags, sealed, and stored at room temperature until processing.

The soil samples were dried in an oven at a temperature of 110 °C for 16 h to remove moisture; the dried samples obtained were then sieved by size through a vertical series of sieves, with meshes from 1 cm to 0.25 mm, obtaining homogeneous samples.

For each soil sample, 50.0 mg of powder was then treated with 4.0 mL of aqua regia (HCl/HNO₃ 3:1) in Teflon crucibles and heated at 200 °C. After 15 min, 2 mL of hydrofluoric acid was added to the mixture and allowed to react; after another 15 min, the remaining 4 mL of aqua regia mixture was added. The mixture was allowed to react for 15 min, then cooled down to room temperature and treated with 2.350 mL of perchloric acid. The yellow solution obtained was diluted to 50.0 mL with ultrapure water in a plastic flask and analyzed.

Samples were treated in triplicate to ensure good reproducibility of results. Data were reported as mean and standard deviation of three measures.

2.3.3. Grape Samples

Seventeen vineyards grown on the soils selected were chosen and classified as follows: NG1, NG2, NG3, NG4, NG5, NG6, NG7, and NG8 from the Canavese region; NG9, NG10, NG13, and NG14 from Langhe; NG11 and NG12 from Aosta Valley; and NG15, NG16, and NG17 from Valtellina.

To better understand the correlations between the soil samples and the grape, must, and wine samples analyzed, it is important to clarify that the progressive numbers N1–N17 identify the individual vineyards under study. For example, NG1, NM1, and NW1 refer to the grape (G), must (M), and wine (W) samples from vineyard N1. Additionally, samples N3, N4, and N5 all come from adjacent vineyards, where only soil S3 could be analyzed through sampling, while samples N6, N7, and N8 come from neighboring plots analyzed as soil S11. Similarly, for the samples from the Langhe region, N9 and N10 come from vineyards of different ages grown on soil S4, while there is a direct correspondence between

soils S5 and S6 and vineyards N13 and N14. Likewise, soils S9 and S10 are the growing locations for vineyards N15 and N16–17, respectively.

Grape samples were collected with a scheme analogous to the one used for soil samples, collecting 10 berries for each bunch located near the point of the soil sample; berries were placed into labeled polyethylene bags, sealed, frozen, and conserved at $-18\text{ }^{\circ}\text{C}$ until analysis. Berries were collected manually at ripening.

For analysis, grapes were crushed with a blender, transferred to crystallizers, and dried in an oven at $110\text{ }^{\circ}\text{C}$ for approximately 24 h; then, the samples were reduced to powder using an agate mortar.

Two different mineralization methods were tested to evaluate their extraction power. The first method involved the use of pure nitric acid and hydrogen peroxide: 1.00 g of grape powder was treated with 2.00 mL of HNO_3 in a Teflon vessel and heated at $100\text{ }^{\circ}\text{C}$, using a water bath, for 1 h. After that, 1.00 mL of H_2O_2 was added to the mixture and allowed to react at $100\text{ }^{\circ}\text{C}$ for 1 h. The treatment was repeated a second time with the same amounts of reagents and timing to achieve the complete mineralization of the sample. The straw-yellow solution was then cooled to room temperature and diluted to 50.0 mL with ultrapure water in a plastic flask.

The second method involved the use of a mixture of HNO_3/HCl 1:3 (aqua regia) and hydrogen peroxide: 1.00 g of grape powder was treated with 2.00 mL of aqua regia in a Teflon vessel and heated at $100\text{ }^{\circ}\text{C}$ using a water bath for 30 min. After that, 1.00 mL of H_2O_2 was added to the mixture and allowed to react at $100\text{ }^{\circ}\text{C}$ for 30 min. The treatment was repeated a second time with the same amounts of reagents and timing to achieve the complete mineralization of the sample. The yellow-orange solution was then cooled to room temperature and diluted to 50.0 mL with ultrapure water in a plastic flask.

Samples were prepared in triplicate for each method to ensure good reproducibility of results. Data were reported as mean and standard deviation of three measures.

2.3.4. Must Samples

To obtain the must, berries were sampled using the same procedure as for the grape analysis (see Section 2.3.3) and then pressed. Each resulting must was analyzed for soluble solid content (22–24 Brix), total acidity (7.50–10.0 g/L, expressed as tartaric acid), and pH (3.10–3.30). The sixteen samples obtained were then treated with a mixture of pure nitric acid and hydrogen peroxide for elemental analysis: 2.00 g of must was treated with 3.0 mL of HNO_3 and 1.0 mL H_2O_2 at $100\text{ }^{\circ}\text{C}$ for three hours; then, the solution obtained was diluted to 50.0 mL with ultrapure water in a plastic flask. All the samples were prepared in triplicate and analyzed. Data were reported as mean and standard deviation of three measures.

2.3.5. Wine Samples

At commercial harvest, grapes were collected from each vineyard selected for the study and treated separately as follows. The grape berries were destemmed and crushed in enological steel tanks. Each must was fermented with *Saccharomyces cerevisiae* yeast, with maceration lasting about 12 days under controlled temperature conditions. After fermentation, the grape pomace was pressed, and the wines underwent malolactic fermentation in steel tanks. At the end of fermentation, a small portion of the wine was filtered, adjusted for free sulfur dioxide (35 mg/L), and bottled in 0.75 L glass bottles. The remaining portion was used by the individual producers for the standard aging procedures in the cellar.

Seventeen bottled wine samples were analyzed without a mineralization step: 5.0 and 25.0 mL of each sample were treated with 2.0 mL of HNO_3 65% in a plastic flask, and diluted to 50.0 mL with ultrapure water to achieve a dilution with a ratio of 1:10 and 1:2, respectively, necessary to analyze all the elements considered.

All the samples were prepared in triplicate for each dilution ratio and analyzed; data were reported as the mean and standard deviation of three measures.

2.3.6. ICP-AES Analysis

Analyses were conducted using Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) with an ICAP 6300 instrument (Thermo Scientific, Waltham, MA, USA) [22]. The emission wavelengths for the elements of interest were selected by optimizing the instrumental parameters to ensure high sensitivity, accuracy, and minimal interference between different element emissions. Their values are listed in Table 2. To ensure reliable repeatability of mineral element analyses, it is essential that the instrument’s operating conditions remain consistent. For these determinations, the following settings were used: torch power of 1350 W, pump speed of 60 RPM, auxiliary gas flow at 0.50 L/min, and nebulization gas flow at 0.25 L/min

Table 2. List of the emissions wavelengths used for elements analyzed by ICP-AES.

Element	Wavelength (nm)	Element	Wavelength (nm)
Al	167.079	Mn	257.079
Ba	233.527	Mo	202.030
Ca	273.690	Ni	221.647
Co	228.616	Sb	206.833
Cr	267.761	Sr	421.552
Cu	324.754	Ti	334.941
Fe	238.204	V	309.311
K	769.896	Zn	213.800
Li	670.784	Zr	343.823
Mg	279.079		

2.3.7. Principal Component Analysis (PCA)

To achieve a more comprehensive assessment of soil characteristics for future comparisons with grapes and wines, we conducted a Principal Component Analysis (PCA) on the collected data. This analysis utilized either the complete dataset of concentrations for all determined elements or specific subsets defined by the average concentrations of individual elements. These subsets were categorized as follows: “*macro elements*”, which include Ca, K, and Mg; “*meso elements*”, comprising Al, Ba, Cu, Fe, Mn, Sr, and Zn; and “*micro elements*”, consisting of Co, Cr, Li, Mo, Ni, Sb, Ti, V, and Zr.

3. Results

3.1. Soil Analyses

The analysis conducted on 11 soil samples (reported in Table 3 as S1, S2, etc.) from the vineyards where grape bunch sampling was performed revealed, as expected, significant differences in the concentrations of various microelements and their distribution based on the geological characteristics of the underlying substrate (Table 3). The examination of individual elements highlights considerable variability depending on the grouping of soil types selected for the analysis.

Table 3. Concentrations of elements in soils, expressed as mg element/Kg soil.

	Ca	K	Mg	Fe	Mn	Zn	Al	Ba	Cu	Mo	Ni	Sb	Sr	Co	Cr	Li	Ti	V	Zr
S1	110.5	19.16	155.4	9.36	1.01	0.86	25.97	8.55	0.84	0.23	0.69	2.83	0.25	0.44	0.23	9.02	0.68	0.23	0.25
S2	129.9	21.81	175.1	9.23	0.98	0.83	11.25	3.67	0.56	0.16	0.45	1.83	0.19	0.48	0.46	10.47	2.70	0.38	0.27
S3	147.7	24.54	171.0	9.94	1.02	0.84	32.52	12.99	0.88	0.24	0.69	2.77	0.37	0.46	0.25	9.47	0.82	0.22	0.26
S4	24.43	28.72	26.55	38.82	1.05	0.48	114.6	4.88	0.99	0.29	0.99	3.34	0.18	0.52	0.51	11.57	2.93	0.42	0.31
S5	20.44	28.35	26.71	36.07	0.99	0.56	104.3	5.18	1.08	0.27	0.94	3.15	0.13	0.50	0.47	10.97	2.88	0.38	0.28
S6	8.80	24.26	19.53	33.72	0.93	0.36	75.38	2.21	0.73	0.15	0.59	1.65	0.10	0.27	0.37	6.03	2.92	0.28	0.15
S7	8.07	23.06	19.31	29.55	0.82	0.32	67.34	3.06	0.68	0.14	0.53	1.50	0.10	0.24	0.32	5.58	2.46	0.24	0.13
S8	12.38	30.30	26.03	35.89	0.97	0.54	103.00	4.26	0.93	0.27	0.94	3.06	0.18	0.50	0.50	10.88	3.17	0.40	0.27
S9	67.99	25.25	140.70	138.50	0.45	1.75	133.10	15.59	4.02	0.36	0.54	4.80	0.23	0.32	0.68	15.49	12.29	0.23	0.75
S10	65.32	25.07	150.30	173.30	0.44	1.61	123.50	16.68	4.47	0.35	0.52	4.63	0.17	0.31	0.63	14.97	12.32	0.22	0.69
S11	4.71	28.94	7.09	22.23	0.69	0.09	12.74	0.80	0.31	0.00	0.10	1.65	0.04	0.01	0.14	1.47	1.87	0.18	nd *

* nd = not detectable.

For instance, focusing on Mg as one of the main elements, we observed a significant difference in concentrations between samples S1, S2, S3, S9, and S10 and samples S4 to S8 (Figure 1a). In contrast, the analysis of Fe (Figure 1b) shows a noteworthy presence of this element in soils S9 and S10, with concentrations ranging from 138 to 173 mg Fe/kg of soil. In comparison, soils S1 to S3 are relatively deficient in Fe, with concentrations around 10 mg Fe/kg of soil. The remaining soils exhibit Fe concentrations within the range of 22.2 to 38.8 mg Fe/kg of soil.

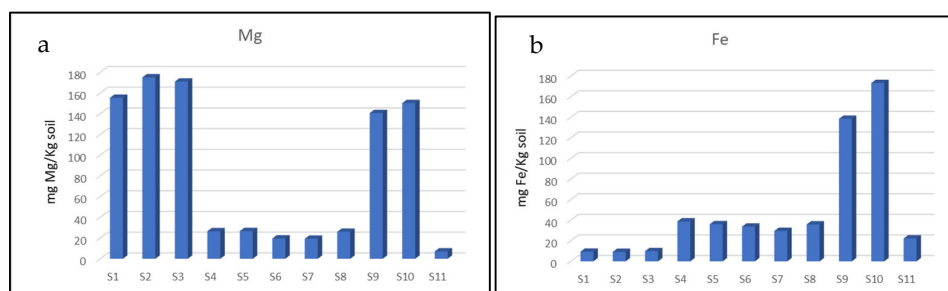


Figure 1. (a) Bar-plot of Mg concentration in analyzed soils, reported as mg Mg/Kg soil. (b) Bar-plot of Fe concentration in analyzed soils, reported as mg Fe/Kg soil.

The PCA performed on the complete dataset (Figure 2a) reinforces the findings from the initial data analysis, revealing a sample grouping that aligns perfectly with earlier observations. Furthermore, it facilitates the categorization of samples based on their actual geographic origins.

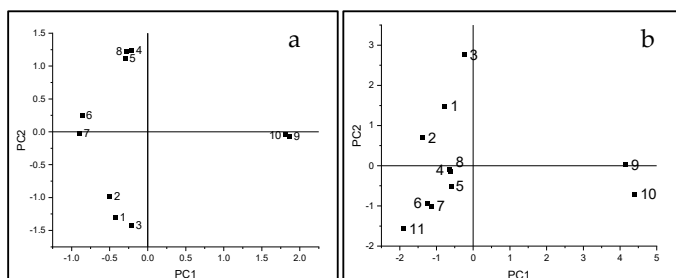


Figure 2. (a) PCA of the complete dataset of elements' concentrations variance PC1 56.0%, PC2 22.3%. (b) PCA performed only on 'meso elements' variance PC1 66.8%, PC2 9.19%.

The same analysis conducted with only the 'meso elements' produced less definitive results (Figure 2b), as it was unable to differentiate all the groups of soils. It could only

distinguish samples S1 to S3, S9, and S10 from the others without providing additional information.

3.2. Grapes Analyses

Selecting a treatment for the grape sample proved particularly challenging due to its complex organic matrix (skins, seeds, pulp) and the extensive information required from the analysis. The two mineralization methods tested yielded comparable results for all the elements analyzed, allowing us to accurately determine the concentration of each element in every sample. Table 4 reports data obtained by treatment with nitric acid and hydrogen peroxide.

The analysis of the data from the 17 grape samples revealed a high concentration of Ca, K, and Mg in the berries, which can be directly linked to their physiological development. The variations in concentration observed for these three elements are not significant enough to be correlated with the soil in which the vineyard was grown, as they are directly influenced by multiple environmental and physiological factors.

Meso elements exhibited greater variability among the different samples. Among these are Ba and Sr, which are recognized as significant for tracing the provenance of wines [22], due to their potential accumulation in the berries through fixation processes in the form of insoluble oxalates [4]. Analyzing the concentration variation of these elements, we observe that Sr shows comparable values among samples NG3, NG4, NG6, and NG8, all from the Canavese area (Piedmont), as well as with samples NG13, NG14, NG15, and NG16, which come from the Langhe and Valtellina regions (Lombardy).

Table 4. Concentrations of elements in grapes expressed as mg element/Kg grapes. Standard deviation was calculated on values obtained from replicated samples.

	Ca	±SD	K	±SD	Mg	±SD	Al	±SD	Ba	±SD	Cu	±SD	Fe	±SD
NG1	1111	49	12,308	654	558.4	8.4	3.24	0.34	3.21	0.16	48.95	1.47	18.03	1.23
NG2	1352	237	10,785	246	567.0	41.1	10.60	0.99	2.01	0.16	18.51	2.30	24.95	5.10
NG3	1262	66	12,626	228	666.7	30.5	6.31	0.40	3.67	0.24	41.92	7.19	26.16	4.84
NG4	1248	37	15,028	771	651.8	22.4	16.01	1.57	3.20	0.57	37.98	3.84	28.95	3.04
NG5	1086	97	9718	258	621.3	12.4	9.74	0.21	6.58	0.54	21.71	0.84	17.37	2.44
NG6	1803	239	11,047	24	635.8	53.6	27.21	0.03	1.61	0.01	40.29	5.67	17.83	1.74
NG7	1811	83	12,386	2307	597.5	8.5	17.03	3.02	1.84	0.07	31.63	3.41	18.18	5.97
NG8	1475	204	16,243	1025	619.0	44.7	10.83	0.57	2.95	0.31	37.94	9.05	26.60	3.47
NG9	1577	100	13,846	819	611.8	29.0	6.97	2.67	1.86	0.37	47.98	5.63	25.99	0.19
NG10	1489	103	13,359	2244	632.4	12.5	7.90	1.75	2.89	0.41	44.55	0.68	25.04	3.17
NG11	1311	77	10,289	435	527.7	59.6	6.08	0.82	1.27	0.07	44.28	2.15	17.85	1.37
NG12	1534	197	14,605	2151	568.0	48.0	15.53	1.42	2.75	0.32	75.92	7.44	28.51	1.94
NG13	1207	70	8813	991	441.7	13.9	11.21	0.89	0.78	0.10	9.95	0.35	26.49	6.50
NG14	1232	5	14,533	1797	472.3	43.7	12.50	2.47	1.22	0.21	9.28	1.85	21.05	1.65
NG15	1268	96	9694	1296	446.0	24.9	8.37	2.10	1.22	0.29	9.29	2.48	14.69	1.45
NG16	1188	88	8653	1120	422.5	23.9	13.78	1.55	1.10	0.21	8.96	1.74	25.16	2.73
NG17	1666	278	10,627	811	508.2	65.3	12.83	4.39	1.44	0.33	11.19	1.17	17.53	3.17

Table 4. Cont.

	Mn	±SD	Sr	±SD	Zn	±SD	Co	±SD	Cr	±SD	Li	±SD
NG1	10.35	0.09	3.18	0.10	9.46	1.97	1.38	0.08	0.77	0.01	0.02	0.00
NG2	12.85	2.22	3.85	0.59	11.84	3.46	1.25	0.17	0.85	0.04	0.04	0.00
NG3	8.05	0.72	4.95	0.39	7.97	1.84	1.40	0.07	0.97	0.15	0.04	0.00
NG4	8.23	0.99	4.69	0.78	7.45	1.36	0.22	0.00	1.12	0.11	nd *	nd *
NG5	21.68	4.29	6.09	0.40	9.73	1.56	0.96	0.09	0.96	0.28	0.06	0.01
NG6	5.99	0.64	4.74	0.98	9.99	4.88	0.27	0.12	0.50	0.07	nd *	nd *
NG7	6.43	0.81	7.46	3.04	10.04	2.71	0.18	0.03	0.47	0.08	nd *	nd *
NG8	12.85	1.77	4.78	0.90	14.63	3.41	0.26	0.07	0.97	0.15	0.03	0.00
NG9	11.35	3.80	3.00	0.17	11.92	2.43	1.56	0.02	1.10	0.34	0.03	0.00
NG10	9.89	0.80	3.60	0.52	12.15	2.64	0.81	0.05	0.81	0.11	0.04	0.00
NG11	2.09	0.32	8.15	1.78	7.54	3.29	1.23	0.12	0.87	0.02	0.03	0.02
NG12	5.54	1.18	3.39	0.70	11.22	4.84	0.21	0.10	0.67	0.09	nd *	nd *
NG13	2.50	0.37	4.67	0.74	7.56	1.06	0.24	0.00	0.46	0.02	nd *	nd *
NG14	4.26	0.85	4.58	0.54	8.00	2.41	0.14	0.02	0.40	0.10	nd *	nd *
NG15	3.98	0.44	5.00	0.59	7.55	1.76	0.82	0.04	0.69	0.09	0.06	0.01
NG16	1.90	0.56	4.12	0.96	6.75	1.78	0.27	0.00	0.52	0.11	nd *	nd *
NG17	4.63	0.86	6.41	2.12	10.68	2.80	0.79	0.01	0.71	0.02	0.07	0.01
	Mo	±SD	Ni	±SD	Sb	±SD	Ti	±SD	V	±SD	Zr	±SD
NG1	0.02	0.00	1.12	0.06	0.08	0.00	0.06	0.01	1.33	0.03	0.70	0.06
NG2	0.02	0.01	0.72	0.11	nd *	nd *	0.21	0.03	1.44	0.15	0.87	0.18
NG3	0.08	0.02	0.65	0.12	nd *	nd *	0.15	0.01	1.56	0.09	0.58	0.12
NG4	0.27	0.04	0.86	0.03	0.11	0.04	0.34	0.09	1.69	0.13	0.25	0.02
NG5	0.02	0.01	0.70	0.07	1.06	0.05	0.28	0.04	1.64	0.05	2.13	0.77
NG6	0.44	0.11	1.39	0.10	0.01	0.00	0.57	0.09	1.83	0.35	0.41	0.03
NG7	0.53	0.02	0.85	0.17	1.43	0.33	0.63	0.07	1.81	0.11	0.36	0.03
NG8	0.08	0.01	1.00	0.18	0.08	0.00	0.35	0.17	1.57	0.09	0.16	0.00
NG9	0.08	0.02	0.79	0.10	0.15	0.01	0.16	0.05	1.28	0.15	1.03	0.48
NG10	0.01	0.00	1.00	0.08	0.21	0.20	0.12	0.01	1.63	0.03	1.32	0.84
NG11	0.06	0.00	0.64	0.09	nd *	nd *	0.21	0.08	1.37	0.14	0.95	0.23
NG12	0.43	0.05	1.17	0.40	0.70	0.44	0.39	0.03	1.51	0.19	0.12	0.01
NG13	0.30	0.01	1.17	0.15	0.86	0.04	0.37	0.02	1.39	0.03	nd *	nd *
NG14	0.47	0.02	0.64	0.16	0.03	0.00	0.62	0.05	1.30	0.13	0.09	0.01
NG15	0.01	0.00	0.53	0.17	1.44	0.13	0.15	0.03	1.20	0.04	2.75	0.09
NG16	0.35	0.03	1.02	0.05	0.96	0.05	0.82	0.08	1.36	0.06	nd *	nd *
NG17	0.02	0.01	0.75	0.19	1.66	0.21	0.19	0.01	1.34	0.11	2.72	0.04

* nd = not detectable.

More significant are the data that deviate from the common average values of the aforementioned samples, such as NG7, NG11, and NG17, which, when correlated with other elements, could provide greater discriminative power. In the case of Ba, we find less variability around only two average values, with exceptions being NG5, which has a markedly higher concentration, and NG13, which has the lowest concentration.

Continuing this type of analysis for all elements in this group, we observed some potentially significant variations; however, when considered individually, they do not allow for accurate discrimination of grape provenance. Even when applying multivariate analysis in this case, definitive results were not achieved. Despite varying the considered elements both by type and total number, the outcomes remained ambiguous (Figure 3a,b).

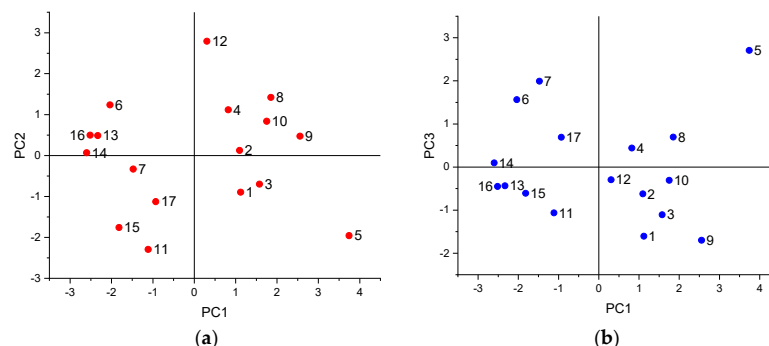


Figure 3. (a) PCA of the complete dataset of elements' concentrations in grapes. (b) PCA performed only on 'meso elements'. (Variance PC1 46.56%, PC2 27.35%, PC3 13.09%).

3.3. Musts Analyses

Table 5 presents the data obtained from the analysis of 16 must samples to evaluate the variation in the quantities of individual elements throughout the production processes. The choice of the Nebbiolo vine is particularly interesting because, due to its unique characteristics and late ripening, it is typically used to produce high-value wines that are vinified almost exclusively as single varietals without the addition of other cultivars. This specific production aspect facilitates the monitoring of potential mineral transfer at every stage without variations arising from factors unrelated to anthropic intervention.

Table 5. Concentrations of elements in musts, expressed as mg element/Kg musts. Standard deviation was calculated on values obtained from replicated samples.

	Ca	±SD	K	±SD	Mg	±SD	Al	±SD	Ba	±SD	Cu	±SD	Fe	±SD
NM1	60.76	2.40	1920.47	33.52	73.00	1.34	0.68	0.06	0.12	0.05	0.79	0.00	12.18	1.57
NM2	76.00	0.14	2040.68	67.94	78.77	1.38	0.91	0.07	0.17	0.05	0.93	0.16	12.89	1.69
NM3	81.00	1.74	1689.78	17.80	91.10	2.93	1.76	0.22	0.12	0.03	1.04	0.38	15.04	2.01
NM4	77.66	0.09	1559.76	16.78	89.99	3.78	1.00	0.00	0.08	0.03	1.03	0.34	12.77	1.68
NM5	76.08	0.91	1806.60	45.75	110.69	3.48	1.63	0.20	0.14	0.04	1.90	0.45	12.10	1.61
NM6	74.37	0.13	1704.38	163.94	101.43	4.90	1.13	0.32	0.11	0.05	0.96	0.14	12.48	1.67
NM7	76.06	2.80	1757.00	34.77	108.31	5.36	1.58	0.40	0.14	0.06	1.88	0.22	13.01	1.78
NM8	86.80	16.39	1715.68	185.11	104.45	16.97	1.63	0.29	0.10	0.06	2.24	0.03	14.09	1.87
NM9	102.21	0.64	1370.71	46.28	89.25	9.16	0.56	0.05	0.12	0.08	0.78	0.23	14.22	1.27
NM10	84.49	10.36	1567.50	316.92	96.91	15.33	1.34	0.53	0.12	0.07	0.77	0.21	16.04	2.25
NM11	110.08	2.45	1363.49	195.63	102.87	6.77	1.07	0.08	0.10	0.02	0.94	0.19	16.24	2.40
NM12	112.94	4.49	1678.54	105.10	106.54	4.65	0.90	0.14	0.09	0.01	1.40	0.39	17.91	2.47
NM13	132.77	21.58	1707.20	25.89	107.33	1.36	0.99	0.18	0.04	0.01	1.34	0.14	16.85	2.24
NM14	109.72	2.95	1584.44	29.76	101.01	7.47	0.99	0.10	0.04	0.01	0.94	0.21	16.47	2.18
NM15	89.83	3.61	1959.78	21.53	86.94	4.48	1.60	0.37	0.11	0.00	1.05	0.21	15.03	2.09
NM16	82.24	0.44	1809.99	61.04	83.43	4.08	1.29	0.30	0.08	0.01	1.06	0.35	14.42	1.93

Table 5. Cont.

	Mn	±SD	Sr	±SD	Zn	±SD	Co	±SD	Cr	±SD	Li	±SD
NM1	1.28	0.10	0.19	0.01	nd *	nd *	0.11	0.03	1.59	0.01	0.05	0.00
NM2	1.55	0.13	0.21	0.01	nd *	nd *	0.12	0.02	1.65	0.04	0.06	0.01
NM3	1.22	0.06	0.21	0.00	0.09	0.01	0.11	0.02	1.65	0.05	0.06	0.00
NM4	1.23	0.07	0.22	0.00	0.08	0.00	0.09	0.04	1.79	0.06	0.05	0.00
NM5	0.96	0.04	0.28	0.00	0.47	0.01	0.12	0.02	2.24	0.11	0.06	0.01
NM6	0.88	0.03	0.26	0.01	0.45	0.01	0.10	0.02	2.31	0.08	0.05	0.00
NM7	0.96	0.11	0.30	0.03	0.18	0.00	0.08	0.01	2.07	0.04	0.05	0.01
NM8	0.92	0.13	0.28	0.01	0.75	0.08	0.09	0.01	2.24	0.11	0.06	0.00
NM9	0.71	0.51	0.26	0.01	0.66	0.02	0.07	0.01	nd *	nd *	0.03	0.00
NM10	0.82	0.15	0.28	0.03	0.66	0.01	0.09	0.01	nd *	nd *	0.05	0.01
NM11	1.17	0.30	0.20	0.06	0.42	0.02	0.07	0.01	nd *	nd *	0.04	0.01
NM12	1.41	0.03	0.23	0.02	0.40	0.02	0.09	0.01	nd *	nd *	0.06	0.01
NM13	0.28	0.01	0.66	0.10	0.30	0.02	0.08	0.02	2.77	0.24	0.06	0.01
NM14	0.35	0.09	0.54	0.20	0.29	0.02	0.08	0.02	3.03	0.12	0.07	0.01
NM15	0.90	0.01	0.20	0.02	0.23	0.01	0.06	0.01	2.65	0.16	0.04	0.01
NM16	0.83	0.03	0.18	0.02	0.23	0.00	0.08	0.00	2.63	0.12	0.05	0.00

	Mo	±SD	Ni	±SD	Sb	±SD	Ti	±SD	V	±SD	Zr	±SD
NM1	0.08	0.00	0.11	0.01	0.04	0.00	0.11	0.00	0.14	0.00	0.16	0.02
NM2	0.09	0.00	0.12	0.00	0.04	0.00	0.11	0.00	0.13	0.01	0.19	0.02
NM3	0.08	0.00	0.04	0.00	0.04	0.01	0.14	0.00	0.16	0.00	0.18	0.02
NM4	0.08	0.01	0.04	0.00	0.05	0.00	0.14	0.00	0.17	0.01	0.16	0.02
NM5	0.11	0.01	0.15	0.00	0.02	0.00	0.12	0.00	0.18	0.00	0.19	0.02
NM6	0.11	0.00	0.15	0.00	0.02	0.00	0.12	0.01	0.18	0.00	0.18	0.02
NM7	0.12	0.01	0.04	0.00	0.04	0.01	0.15	0.01	0.20	0.01	0.18	0.02
NM8	0.12	0.00	0.05	0.00	0.04	0.01	0.14	0.01	0.18	0.02	0.20	0.02
NM9	0.11	0.01	0.19	0.00	0.05	0.01	0.19	0.00	0.13	0.07	0.03	0.00
NM10	0.13	0.01	0.18	0.01	0.05	0.00	0.19	0.01	0.19	0.03	0.04	0.00
NM11	0.03	0.01	0.11	0.01	0.04	0.01	0.14	0.01	0.19	0.02	0.04	0.00
NM12	0.03	0.00	0.11	0.01	0.04	0.01	0.15	0.00	0.19	0.01	0.19	0.02
NM13	0.13	0.01	0.21	0.00	0.01	0.00	0.12	0.00	0.19	0.01	0.05	0.00
NM14	0.13	0.01	0.19	0.02	0.01	0.01	0.12	0.00	0.20	0.01	0.05	0.00
NM15	0.15	0.01	0.07	0.01	0.02	0.00	0.12	0.00	0.17	0.01	0.03	0.00
NM16	0.14	0.01	0.07	0.00	0.02	0.01	0.11	0.00	0.16	0.01	0.03	0.00

*nd = not detectable.

The first observation was the sharp reduction in the concentrations of Ca, K, and Mg from the berries to the must, likely due to the loss of the solid fractions of skins, seeds, and pulp. Continuing the analysis with the *meso elements*, we noted a similar trend to what was partially observed in the grapes, although with absolute values lower than those previously recorded. The concentration variations were somewhat pronounced but could be weakly correlated with factors related to growth conditions. A similar conclusion could be drawn

from the analysis of *micro elements*, which show less variability among the different samples and may, therefore, be less discriminative for our investigation.

Applying multivariate analysis solely to the dataset concerning the *meso elements* (Figure 4) confirmed these observations, as PCA revealed a distribution of samples that correctly groups many from the Canavese (red oval), some from the Langhe (green square), and those from the Valtellina (blue oval). Notably, the must samples NM6, NM11, NM12, NM9, and NM10 are exceptions; however, the last two, also from the Langhe, are positioned closely together.

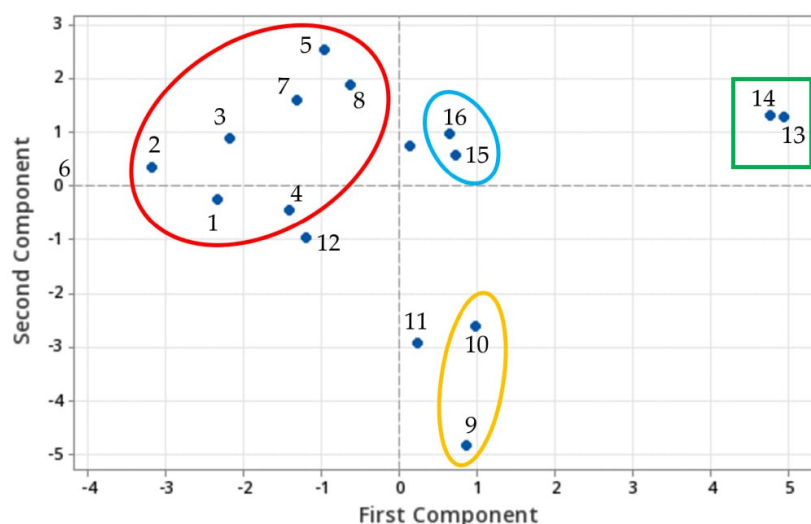


Figure 4. PCA of must elemental concentrations (PC1 57.47%, PC2 31.09%).

3.4. Wine Analyses

The analysis of the wines was conducted to assess the changes in mineral composition that occurred during the complete vinification process. The data obtained, presented in Table 6, show a significantly greater reduction in the concentrations of the main abundant elements—Ca, K, and Mg—consistent with the complete elimination of the solid fraction. The concentrations of all other elements considered were also significantly reduced, partly due to the fact that the analyses were performed on the matrix as it was, following simple acidification but without any further pretreatment. As a result, the analysis focused on diluted aqueous solutions, leading to a reduction in the actual concentrations. Another potential cause for this reduction is the production methodology, during which the particulate fraction is progressively removed, leaving only the liquid fraction. Consequently, a detailed evaluation of the variations in individual elements proved to be ineffective, prompting us to apply multivariate analysis to these datasets as well.

In this case, PCA produces meaningful results, successfully grouping the wines according to their origin using only the dataset of “*micro elements*”—those found in trace amounts, such as Co, Cr, Li, Mo, Ni, Sb, Ti, V, and Zr (Figure 5). The use of both the complete dataset and the “*meso elements*” allows for correct grouping of wines from the Canavese and Valtellina, as previously observed for the grapes. However, it is less effective in grouping the other wines considered.

Table 6. Concentrations of elements in wines expressed as mg element/Kg wine. Standard deviation was calculated on values obtained from replicated samples.

	Ca	±SD	K	±SD	Mg	±SD	Al	±SD	Ba	±SD	Cu	±SD	Fe	±SD
NW1	3.21	0.67	41.27	1.32	2.62	0.23	1.85	0.07	0.12	0.00	0.53	0.00	0.31	0.01
NW2	2.43	0.63	55.38	9.74	2.44	0.48	1.76	0.11	0.12	0.01	0.53	0.02	0.29	0.01
NW3	8.10	3.69	94.33	33.09	5.27	2.41	2.26	0.03	0.16	0.00	0.74	0.01	0.36	0.01
NW4	3.19	1.49	56.92	6.04	2.55	0.55	1.80	0.06	0.13	0.00	0.53	0.01	0.28	0.01
NW5	3.17	2.03	60.08	0.67	1.14	0.11	1.75	0.08	0.11	0.01	0.88	0.03	0.27	0.01
NW6	2.78	0.89	31.96	4.42	1.49	0.18	2.00	0.02	0.12	0.00	0.65	0.01	0.32	0.00
NW7	1.32	0.00	57.16	5.46	1.18	0.08	2.04	0.70	0.11	0.01	0.59	0.04	0.28	0.00
NW8	3.99	0.05	44.75	3.40	3.18	0.58	1.72	0.07	0.10	0.00	0.53	0.01	0.27	0.00
NW9	4.21	1.11	88.54	10.61	1.93	0.47	1.83	0.07	0.12	0.00	0.95	0.06	0.36	0.02
NW10	1.17	0.03	42.51	1.39	1.65	0.06	1.58	0.05	0.09	0.00	0.47	0.01	0.46	0.20
NW11	2.43	0.45	74.12	7.23	1.89	0.24	1.71	0.04	0.11	0.00	0.77	0.04	0.29	0.02
NW12	2.91	0.10	67.11	4.36	1.94	0.30	1.68	0.00	0.10	0.00	0.52	0.01	0.29	0.00
NW13	3.88	0.86	37.68	3.44	2.25	0.18	2.38	0.17	0.14	0.01	0.64	0.03	0.30	0.00
NW14	2.89	0.33	50.16	2.46	2.01	0.22	2.24	0.12	0.14	0.01	0.84	0.01	0.31	0.02
NW15	3.43	0.33	45.54	4.38	2.64	0.40	2.35	0.02	0.14	0.00	0.66	0.01	0.30	0.00
NW16	2.83	0.58	73.90	2.52	1.93	0.15	1.64	0.09	0.10	0.00	0.79	0.06	0.30	0.02
NW17	3.08	0.06	42.70	2.15	2.92	0.14	2.41	0.00	0.14	0.00	0.65	0.00	0.33	0.00
			Mn	±SD	Sr	±SD	Zn	±SD	Co	±SD	Cr	±SD	Li	±SD
NW1			0.08	0.00	0.03	0.00	0.03	0.01	0.17	0.00	0.16	0.00	0.36	0.00
NW2			0.14	0.02	0.03	0.00	0.03	0.01	0.16	0.00	0.16	0.01	0.35	0.00
NW3			0.12	0.04	0.06	0.02	0.09	0.02	0.21	0.01	0.22	0.01	0.42	0.01
NW4			0.18	0.03	0.03	0.00	0.04	0.01	0.17	0.00	0.16	0.00	0.36	0.00
NW5			0.05	0.00	0.02	0.00	0.10	0.10	0.17	0.01	0.16	0.00	0.36	0.00
NW6			0.11	0.01	0.04	0.00	0.05	0.01	0.16	0.00	0.15	0.00	0.35	0.00
NW7			0.05	0.00	0.03	0.01	0.05	0.03	0.16	0.00	0.16	0.00	0.36	0.00
NW8			0.06	0.00	0.04	0.00	0.03	0.01	0.19	0.00	0.19	0.00	0.40	0.00
NW9			0.04	0.01	0.06	0.01	0.09	0.08	0.16	0.00	0.17	0.01	0.35	0.00
NW10			0.07	0.00	0.03	0.00	0.02	0.00	0.15	0.00	0.15	0.01	0.33	0.01
NW11			0.06	0.01	0.03	0.00	0.02	0.00	0.16	0.00	0.16	0.00	0.35	0.00
NW12			0.06	0.00	0.03	0.00	0.02	0.01	0.16	0.00	0.15	0.00	0.35	0.00
NW13			0.06	0.00	0.04	0.00	0.05	0.01	0.22	0.01	0.20	0.01	0.45	0.02
NW14			0.06	0.00	0.03	0.00	0.05	0.01	0.20	0.02	0.19	0.01	0.42	0.03
NW15			0.06	0.01	0.03	0.00	0.05	0.01	0.22	0.00	0.20	0.00	0.45	0.00
NW16			0.06	0.01	0.03	0.00	0.03	0.00	0.15	0.00	0.16	0.01	0.34	0.00
NW17			0.07	0.00	0.03	0.00	0.07	0.02	0.22	0.00	0.21	0.00	0.45	0.00

Table 6. Cont.

	Mo	±SD	Ni	±SD	Sb	±SD	Ti	±SD	V	±SD	Zr	±SD
NW1	0.79	0.01	0.57	0.00	2.46	0.02	0.07	0.00	0.07	0.00	0.17	0.00
NW2	0.82	0.09	0.54	0.02	2.41	0.09	0.07	0.00	0.08	0.01	0.17	0.01
NW3	1.05	0.04	0.71	0.01	3.10	0.09	0.09	0.01	0.15	0.01	0.24	0.02
NW4	0.82	0.01	0.56	0.01	2.50	0.04	0.07	0.00	0.08	0.00	0.18	0.00
NW5	0.81	0.12	0.53	0.06	2.35	0.24	0.07	0.00	0.07	0.01	0.17	0.01
NW6	0.76	0.01	0.54	0.01	2.39	0.05	0.06	0.00	0.07	0.00	0.17	0.01
NW7	0.78	0.02	0.54	0.01	2.45	0.05	0.07	0.00	0.07	0.00	0.17	0.00
NW8	0.92	0.01	0.64	0.00	2.84	0.02	0.08	0.00	0.12	0.01	0.21	0.00
NW9	0.88	0.01	0.56	0.01	2.45	0.00	0.07	0.00	0.09	0.00	0.17	0.00
NW10	0.75	0.03	0.51	0.01	2.23	0.06	0.06	0.00	0.06	0.01	0.15	0.01
NW11	0.86	0.00	0.56	0.00	2.44	0.01	0.07	0.00	0.08	0.00	0.17	0.00
NW12	0.76	0.01	0.53	0.00	2.34	0.02	0.06	0.00	0.07	0.00	0.16	0.00
NW13	0.93	0.03	0.72	0.04	3.27	0.18	0.10	0.01	0.13	0.02	0.27	0.02
NW14	0.86	0.06	0.72	0.02	3.02	0.26	0.09	0.01	0.10	0.02	0.24	0.03
NW15	0.92	0.01	0.72	0.01	3.25	0.04	0.10	0.00	0.13	0.00	0.27	0.00
NW16	0.80	0.03	0.53	0.02	2.32	0.06	0.06	0.00	0.07	0.00	0.16	0.00
NW17	0.95	0.02	0.74	0.01	3.33	0.02	0.10	0.00	0.13	0.00	0.27	0.00

*nd = not detectable.

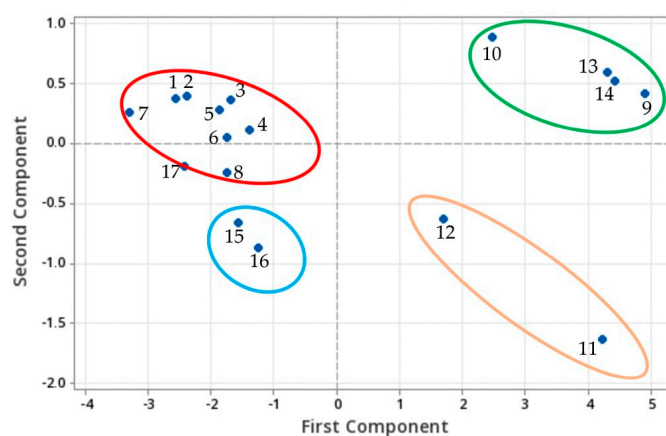


Figure 5. PCA of wine elemental concentrations (PC1 59.95%, PC2 25.56%). Wines are divided based on their provenance: Canavese (red oval), Langhe (green oval), Valtellina (blue oval), and Aosta Valley (orange).

4. Discussion

The relationship between the geological substrate and the mineral composition of grapes and wine has been widely studied in the literature as a potential method for wine traceability; this approach can both enhance the final product value and serve as a tool for detecting fraud [27–29]. Specifically, the analysis of alkali and alkaline earth metals, as well as transition metals available to the plant, has often highlighted certain elements—particularly Ba, Rb, and Sr—as promising candidates for assessing the origin of wine [28].

In our study, the analysis of soil samples from different vineyards revealed significant differences in the concentrations of microelements, which correlate with the geological characteristics of the underlying substrate. The notable variability in the concentrations of

key elements, especially magnesium and iron, across soil, grapes, and wines underscores the influence of soil characteristics on the elemental availability in grapes. These findings extend the implications of results previously reported in the literature [22].

Moreover, it is well established that geological diversity within vineyard regions plays a crucial role in shaping the nutrient profile of soils, which can directly influence vine health and grape composition [30]. Additionally, soil composition can affect the sensory attributes of wine, further emphasizing the connection between terroir and wine quality [4].

It is well known, for example, that high pH and clay-rich soils are particularly beneficial for improving grape quality [4,22], and that with these soil characteristics, Ba, Sr, and Mg are more available to plants, while the availability of microelements such as Si, Ti, Mn, and V could be favored by total soil concentration or lower pH. However, the foliar and berry content is also influenced by the reciprocal interactions between elements, as well as by specific genetic resistance mechanisms that are activated when elements with potentially toxic effects on plants, such as Ba, Mn, and Sr, become excessively concentrated in the soil's nutrient solution. Therefore, the high bioavailability of a specific element in soil does not necessarily result in a high concentration of that element in plant tissues [22].

Principal Component Analysis (PCA) provided additional insights into the relationships among soil samples. The successful grouping of samples based on geographic origins reinforces the idea that distinct terroirs can be characterized by their mineral profiles. However, PCA applied to *mesoelements* gave few relevant results in soils, as these elements were not sufficient to allow a complete differentiation of the origin of the soils themselves, while a better separation was obtained when considering the whole pattern of elements considered. This variability may reflect the complex interactions between different elements and their collective impact on vine growth [31].

The challenges encountered in analyzing the grape samples arose from the complexity of their organic matrix. However, the mineralization methods used were effective in providing accurate elemental analysis, which revealed that the abundance of Ca, K, and Mg in the grape samples should be attributed to their physiological growth conditions rather than the composition of the soil. This observation underscores the fact that while *macroelements* are essential for vine development, their concentrations in the berries may not serve as reliable indicators of soil provenance [32].

Conversely, *mesoelements* such as barium (Ba) and strontium (Sr) showed greater variability, highlighting their potential as markers for wine provenance due to their accumulation in grapes as insoluble oxalates [22]. The relatively consistent Sr values across several samples from the Canavese region indicate that certain areas may impart unique mineral signatures to the grapes, which could be useful for tracing wine origins.

However, the inability to achieve definitive results for grape provenance through individual element analysis suggests that a multifaceted approach is necessary. Variations in Ba concentrations were limited, with only a few samples deviating significantly from average values, which may not provide sufficient discriminative power. These challenges underline the complexity of grape composition and the need for robust analytical techniques to better correlate mineral content with geographical origins [33].

The analysis of must samples showed a pronounced reduction in the concentrations of Ca, K, and Mg, likely due to the loss of solid components during processing. This decline raises questions about mineral transfer throughout winemaking and how it affects the final product. While some trends observed in *mesoelements* were consistent with those in grape samples, the lower absolute values suggest a shift in mineral availability during fermentation.

The application of PCA to the must samples corroborated previous findings, effectively grouping samples from distinct regions. However, exceptions in sample positioning high-

light the nuances of mineral transfer processes and the influence of vinification techniques on elemental composition.

Finally, the analysis of wines indicated significant reductions in priority elements, echoing trends observed in musts. The effectiveness of PCA in grouping wines based on *microelements* suggests that these components may play a crucial role in defining wine character and provenance. However, the less successful grouping of wines based on *mesoelements* underscores the complexity of wine composition and the need for further investigation into the interactions among various elements during the fermentation process.

The overall analysis of the results revealed a relationship between the concentrations of plant-available cations in the studied soils and the compositions of the grapes, grape musts, and wines. All the cations analyzed generally showed higher concentrations in grapes compared to the soils, with progressively lower concentrations found in the grape musts and wines. This result aligns with previous findings in the literature, such as those by Suhaj et al. [28], who, in their study of elemental composition during wine-making, highlighted the progressive decrease in elemental concentrations in the liquid fractions, coupled with an enrichment in the solid phases, such as the must cake and yeast lees, which were then removed in further stages of production.

Notably, the concentrations of Ca, Sr, and Ba were most strongly associated with the organic composition of the grapes [29,30], as outlined, for example, by McKenzie et al. [30], who, in their study, hypothesized the direct influence of the presence of these bivalent cations on metabolic reactions and ion exchange processes within plant cells. For this reason, an intriguing direction for future research could be the analysis of the wines characterized at the elemental level in this study to assess potential variations in the development of organic compounds such as sugars, polyphenols, tannins, and anthocyanins, which may be linked to their mineral composition. For instance, NW3 and NW9, which exhibited higher levels of both Sr and Ba compared to the other samples, are expected—based on the literature—to show different patterns in the development of polyphenols, anthocyanins, and tannins, compared to NM15 and NM17, which had high Ba concentrations but relatively low Sr levels.

5. Conclusions

Overall, this analysis illustrates the intricate relationships between soil, grape, must, and wine compositions, highlighting the significant impact of geological characteristics on elemental availability. While certain elements show promise for tracing provenance, the complexities of biological and environmental interactions necessitate a multifaceted approach to fully understand their implications in viticulture. Future studies should aim to refine analytical techniques and explore the synergistic effects of different elements to enhance our understanding of this specific terroir and its influence on wine quality.

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