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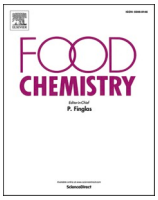

Elemental profile and enological characteristics of *Vitis vinifera* L. cv. Aglianico grapes from a quality wine terroir in southern Italy: relationship with soil composition and chemical properties

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ABSTRACT

Pedoenvironmental factors play a key role in winegrape quality. In five vineyards, elemental profiles (B, Ca, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Si, Sr, Zn) of grape seeds, pulp, skin, and wine-like-juice (WLJ) (except S), and soil element content (NH_4OAc extraction) were analyzed by Inductively-Coupled-Plasma Optical-Emission-Spectrometry. ANOVA showed homogeneity of grape and soil composition across vineyards. Bioconcentration factors (BFs) indicated Fe, B, Zn, Cu uptake from soil to all grape tissues. Significant correlations between grapes and WLJ element content suggested K, Mg, Na, Si, Sr preferential transfer from pulp and skin to WLJ. Principal Component Analysis highlighted correlations between BFs of Cu, Mn, Na, P, S, Si, Zn, Li, and grape pH, WLJ anthocyanins, tannins and total phenols, measured spectrophotometrically, with peculiar soil properties, including electrical conductivity, exchangeable Na and K, silt fraction, pH, carbonates, indicating a terroir control on grape element uptake and quality traits.

1. Introduction

World wine production in 2024, excluding juices and musts, is estimated at 225.8 mhl (million hectolitres) and marked a contraction of nearly 11.2 mhl (−4.8 %) compared to 2023 (OIV, 2025). In 2024, the global vine and wine sector faced a challenging year, marked by adverse climatic conditions causing historically low production levels (OIV, 2025).

A potential issue for wine quality is represented by metal excess. Although potassium, Ca, Mg, and Na are generally present in relevant amounts in wines and do not create toxicological problems, they are found to affect the organoleptic properties and stability of wines, or create simple wine faults (Waterhouse et al., 2016). Excessive levels of K in grapes have been found to harm the quality of the produced wine, since it enhances the concentration decrease of free tartaric acid by precipitation of potassium bitartrate, during the winemaking process (Mpelasoka et al., 2003). The resulting pH increase (> 3.7) causes instability in wine, leading to oxidative and microbiological damages that affect the color intensity and other organoleptic properties of the final product (Mpelasoka et al., 2003). Less common are the Ca tartrate crystals (McKinnon et al., 1994). Magnesium does not directly cause wine faults, but there are some indications that its content may be important in tartrate stability and the taste of wine (Themelis et al., 2001). The wines with a high Na concentration are described as salty, flat, dull, soapy, seawater-like, and brackish (Walker et al., 2010). Silicium in wine, as due to the treatment of grapevine plants with Si during the ripening, has been found to reduce wine oxidation, levels of acetic acid, acetaldehyde, ethyl acetate, and diacetyl, and it should be considered as positive from a sensory point of view (Losada et al., 2022). Other metals, including Al, Cu, Fe, Ni, and Zn, contribute to the haze formation and the change of wine color, as they tend to form complexes with anthocyanins and tannins (Esparza et al., 2005). Iron, Mn, and Cu, to a certain extent in wine, can affect oxidation and reduction processes (Danilewicz, 2016), other than the acetaldehyde formation. Copper, Fe, and Mn form stable complexes with amino acids and polyphenols during wine maturation and storage, influencing aging characteristics, final aroma, taste, and the wine color. Iron is known to be a catalyzer of the chemical reactions involving acetaldehyde and phenolic compounds (Tariba, 2011).

In the wake of the perception that juice, must, and wine quality traits, also including their element content, are strongly influenced by the grape berry mineral composition, in the last two decades

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investigations on the nutrient status of grapes have become a growing concern not only for viticulturists but for oenologists and winemakers, too (Rogiers et al., 2006).

Basic studies on the biological role of nutrients (N, P, K, Ca, Mg, S, B, Zn, Cu, Mn, Fe, Ni, Mo, and Cl) and beneficial (Na, Si, Co) elements (Mengel & Kirkby, 2004; Rogiers et al., 2006), essential for vine nutrition, have focused on their quantification in berries across the soil-plant system (Castillo et al., 2021) and during ripening of grape berries (Bertoldi et al., 2011; Rogiers et al., 2006). Other works have investigated the geochemical relationship between grape berries and soils, analyzing major and trace elements (Protano & Rossi, 2014). In the soil-grape-wine system, data on the relationship between plant tissue composition and total soil element content were reported for five different vineyards in USA and used for inferences on transfer processes of nutrients (Ca, K, Mg, Mn, Cu, Zn) and toxic elements (As, Cd, Pb) (Richardson & Chase, 2021). In this context, the authors calculated bioconcentration factors (BFs) of elements in grape tissues to determine elemental transfer from soil (considering the total soil element content by HNO_3-HF total digestion) to the grapes. Results showed a lack of correspondence between plant tissues and soil element content, and a disconnect governing their accumulation was evidenced. In the field of environmental risk assessment, the BF is a key parameter that describes the ability of plants to accumulate elements from a substrate and is frequently applied for quantitative information on metal uptake, mobilization, and storage (Wu et al., 2011). The BFs can be calculated for each plant part, including roots, stems, leaves, etc. (Zhang et al., 2002). Single extraction procedures are recommended to assess the bioavailability of major and trace elements from agricultural soils (Milićević et al., 2018), since they allow estimation of mobile or potentially mobile amounts of elements and are suitable for inferences on plant uptake.

Apart from nutrients and beneficial elements content, the essential characteristics of wine quality, including color, aroma, and flavor, are strongly influenced by grape phenolic compounds (Setford et al., 2017). Polyphenols are secondary plant metabolites synthesized during the development of the grape berries, particularly during ripening. For this reason, berries represent the major source of phenolics for must and wine (Gutiérrez-Escobar, Aliaño-González, & Cantos-Villar, 2021).

Although the elemental composition and main phenolic compounds both play a central role in determining grape and wine quality traits, little research has investigated their reciprocal relationship and possible correlation with the soil. In addition, no studies have yet explored the potential link between the process of element uptake in the grape tissues from the soil and both grape phenolic composition and soil properties.

The research work presented here was carried out in the Taurasi DOCG (denomination of origin controlled and guaranteed) wine terroir, selected for its uniqueness in terms of red wine quality production of the Campania Region (southern Italy). This study focused on the elemental composition of *Vitis vinifera* L. cv. Aglianico grapes, used in single variety for the Taurasi wine production, and on the vineyard soils. The main objective was to investigate the possible relationship between the grape characteristics (including phenolic compounds and enological parameters), the uptake of elements by the plant from the soil, and the soil properties. The objective was to formulate hypotheses about how metal bioconcentration in grapes may influence their quality traits. Within this framework, we also focused on i) the element profile of grape seeds, pulp, and skin, to identify which tissue acts as the preferential sink for elements that could negatively affect wine's taste and aroma, aging potential, and color, ii) the possible transfer of elements from the grapes to wine, to assess the role of the different grape tissues as sources of elements in the final product.

2. Materials and methods

2.1. Study area

Five vineyards (Fig. 1), belonging to the terroir production area of the Taurasi DOCG (TA) wine, have been selected in two villages (Montemarano and Mirabella Eclano) of the Avellino province, in very similar and close pedo-environments, approximately 60–80 km north-east of Naples (Table 1). The Taurasi wine has been the only DOCG red wine of the Campania Region for years, and in 2011 was joined by the Aglianico of Taburno DOCG. The vineyards of Boccella (TA-B), Siano (TA-S), and Adelina (TA-A) are close to the Montemarano village, and their reciprocal distance is no longer than 3.5 km. These vineyards have been chosen because they share similar environmental factors, such as altitude (from 446 to 630 m above sea level), slope (16 % on average), and exposure (NE), since these factors are expected to influence grape composition. Then, a bit farther (15 km), but still in the Taurasi DOCG terroir, two additional vineyards at Mirabella Eclano, named TA-O and TA-Y vineyards, have been selected on the same hill at 370 m asl, with NW and SE exposures, respectively. The SE-oriented vineyard was also selected to identify the possible effect of the vineyard exposure, in the same environment, on the relationship between grape composition and soil properties.

The Taurasi terroir is situated in an agricultural area with a centuries-old tradition of viticulture. Vineyard management is under organic farming, and only copper and sulphur-based fungicides are applied, so these elements measured in the vineyard soil must be considered as anthropogenic. From the geomorphological point of view, the TA sites are located in the inner hilly relieves close to the Apennine chain made up of turbidite sediments (flysch) characterised by alternating marly-arenaceous, marly-calcareous, and clayey levels, sometimes covered by ashes and pumices derived from Phlegrean Fields and Somma-Vesuvius volcanoes (di Gennaro A., 2002, provided in Appendix B. Supplementary material). Soils are classified as Haplic Calcisols, Calcaric Cambisols, Calcaric Regosols, and locally Vitric Andosols (FAO, 1998).

2.2. Soil analyses

Appendix A (Supplementary material) provides details on the reagents and buffers used for the soil analyses. Appendix B (Supplementary material) includes references on the methods applied for the soil analyses.

2.2.1. Sampling and analyses of the chemical and physical properties

Soil sampling was performed at 4 points for each vineyard, in triplicate at each point (total 12 points at a vineyard). To maximize the within-vineyard differences among the soils, we considered erosional processes as the main factor driving soil variability, and the sampling focused on both higher and lower altitude zones of the vineyard. For each sampling point, the soil was collected from three depths, i.e., 0–30 (topsoil), 30–70 (mineral soil horizon), and 70–100 cm (bottom soil), for a total of 180 sampled soils. The investigated soil depth was defined according to field observations on soil profiles showing most roots within the upper 80 cm (unpublished results from Caputo A. PhD thesis, 2025). Soils were sampled by a stainless-steel hand auger, mixed within the defined depth, and the composite sample (approximately 500 g) was put in a plastic bag. The applied procedure agreed with the IAEA guidelines (IAEA, 2004). Soil, after drying (30 °C) and sieving (< 2 mm), was analysed according to IUSS Working Group WRB (2022), which provides recommended analytical procedures to be used for soil characterisation, referring to Van Reeuwijk (2002) and USDA (Soil Survey

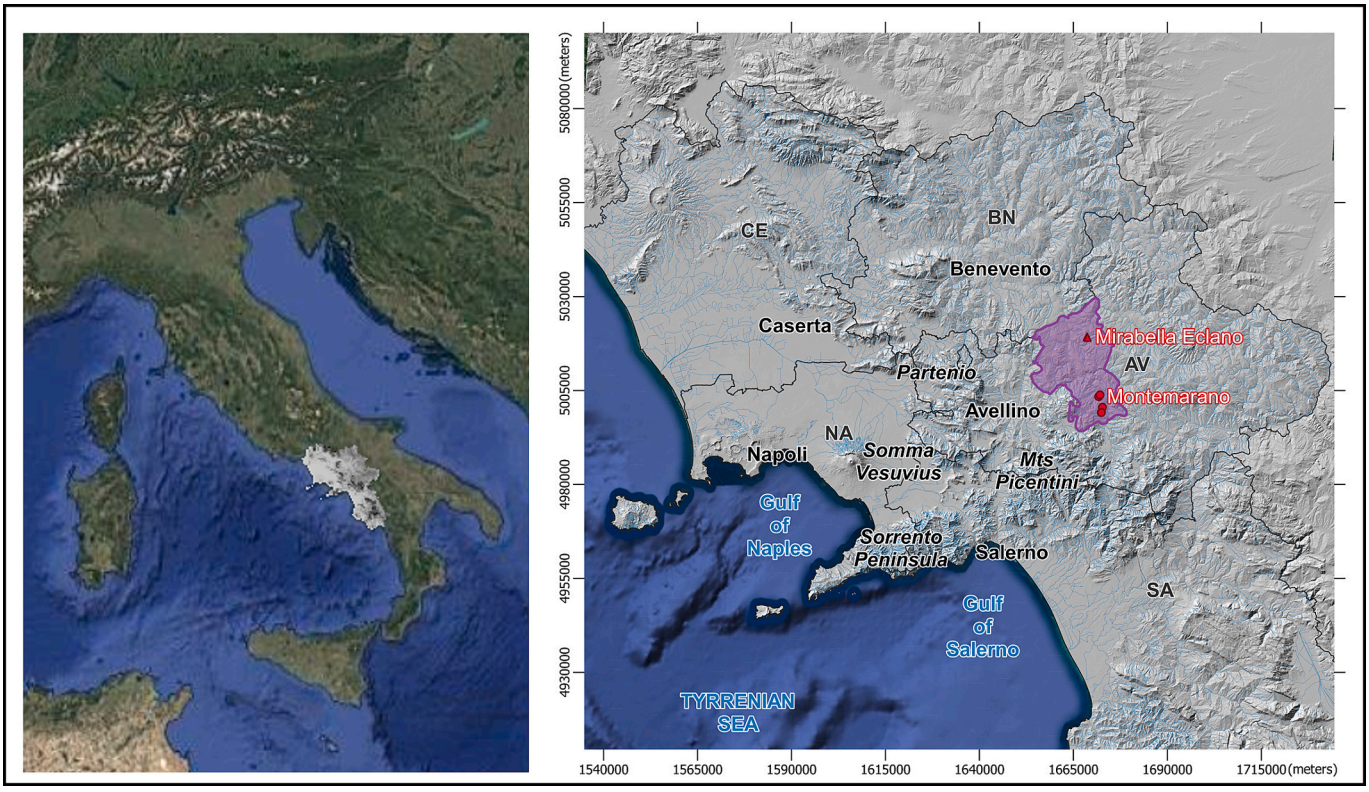

Fig. 1. Location of the vineyards within the study area in the Taurasi wine terroir (southern Italy).

Staff, 2014). The pH was potentiometrically measured in the supernatant suspension 1:2.5 soil:water (*m/v*) ratio by XS model pH 8 meter with glass electrode, electrical conductivity (EC) on soil:water ratio 1:5 (*m/v*) by XS instruments COND7 conductivity meter, organic carbon (OC) content by Walkley-Black procedure (Nelson & Sommer, 1982), available phosphorous by Olsen & Sommers (1982), total carbonates with Dietrich- Fruhling calcimeter by volumetric determination of CO_2 developed by hydrolysis with 6 M HCl, cation exchange capacity (CEC) using barium chloride solution buffered at pH = 8.2 and exchangeable cations (Ca_{ex}, Mg_{ex}, Na_{ex} and K_{ex}) measured by ICP-OES 7400 iCAP Thermo Fisher, particle size distribution (sand, silt and clay fractions) with pipette method by sieving and sedimentation after dispersion with 4 % $(NaPO_3)_6$. The exchangeable sodium percentage (ESP) was calculated as the percentage ratio between Na_{ex} and the CEC (IUSS Working Group WRB, 2022).

2.2.2. Total and bioavailable element content

Total soil element content was analysed in laboratory conditions using a Delta Professional (Olympus, DPO-4000, Waltham, MA, USA) portable X-ray fluorescence spectrometer (pXRF) featuring a Ta X-ray tube operating at 15–40 kV with an integrated large area silicon drift detector (165 eV) and 8 mm^2 window. Fourteen elements, including As, Cr, Cu, Mn, Nb, Pb, Rb, Sr, Th, Ti, V, Y, Zn, and Zr, were analysed in Soil mode, and 5 elements (i.e., Al, Ca, Fe, K, Si) in Mining mode. Measurements were carried out on smooth, uniform surfaces completely in contact with the instrument to minimize surface effects. One hundred eighty air-dried (30 °C) and sieved (< 2 mm) soil samples were analysed in triplicate, inside small cylindrical containers (height = 25 mm; diameter = 30 mm), supplied by the manufacturer (Olympus Corporation) for a total of 540 analyses in each mode. Accuracy of the soil total element content was checked during the soil sample acquisition by analyzing 15 times both NIST 2710a (National Institute of Standards and Technology, 2003) and NIST2711a (National Institute of Standards and Technology, 2022) certificate materials, under the same conditions of the soil analyses.

Soil bioavailable elements (Ca, Mg, K, P, S, Si, Na, Cu, Sr, Zn, Fe, Mn, B, Ni, Li) were determined after single extraction with 1 mol L^{-1} NH_4OAc solution at pH 7. This is a modified version of the method 9 reported by Van Reeuwijk (2002). Analyses were performed on dried and sieved (< 2 mm) soil samples, in triplicate, with a soil-to-solution extraction ratio of 1:8 (*m/v*). Samples were shaken for 120 min using an end-over-end shaker. After centrifugation (5 min at 4100 rpm), solutions were filtered with Whatman quantitative filter paper (ashless, grade 42), recovered in plastic bottles, and stored at 4 °C until spectrometric elemental analysis. Calcium, Mg, K, P, S, Si, Na, Cu, Sr, Zn were determined on 1:5 (*v/v*) dilution ratio solutions, while Fe, Mn, B, Ni, Li on 1:1 (*v/v*) dilution ratio solutions. Ultra-pure Milli-Q water was used for all preparations, including sample dilution. Concentrations of elements were measured by ICP-OES (iCAP 7400 Analyzer - Thermo Fisher Scientific, USA). Standard concentration for the calibration lines was defined according to the element concentration measured at an earlier stage on a mixed sample made by 30 soil extracts. A recovery test to evaluate the accuracy of the extraction procedure was performed using spike solutions. Blank samples were included in each procedure, and both LODm (method limit of detection) and LOQm (method limit of quantification) were calculated by summing to the mean of six analytical blanks (prepared and diluted in the same way as the samples) 3 and 10 times the standard deviation, respectively (Moosavi & Ghassabian, 2018).

2.3. Grape analyses

Appendix A (Supplementary material) provides details on the reagents and buffers used for the grape analyses. Appendix B (Supplementary material) includes references on the methods applied for the grape analyses.

Table 1
Location and environmental data of the Taurasi (TA) sites. *Altitude was referred to the middle slope.

Sites	Village	Province	Altitude*	Exposure	Coordinates		Geomorphological system	Geology of the substrate	Soil classification	Rootstock	date of harvest
			m a.s.l.		Latitude	Longitude					year 2020
TA-A			446	N/NE	40°56′31.74″N	15° 1′13.92″E			D34. Haplic Calcisols, Calcaric Cambisols, Calcaric Regosols	Kober 5BB	October 21st
TA-B	Montemarano	AV	589	NE	40°55′13.36″N	15° 1′31.57″E				420 A	October 21st
TA-S			630	NE	40°54′37.12″N	15° 1′25.15″E	D. Inner hilly reliefs	D3. Marly-arenaceous and calcaric-marly hills		1103P	October 22nd
TA-O	Mirabella		336	NW	41° 2′48.63″N	14°59′22.39″E			D33. Haplic Calcisols, Calcaric Cambisols, Calcaric Regosols, Vitric Andosols	1103P	October 6th
TA-Y	Eclano	AV	370	SE	41° 2′44.55″N	14°59′25.43″E				1103P	October 6th

2.3.1. Sampling and enological characteristics

Grape samples were collected at harvest in October 2020 to capture the element concentration in the berries used for viticulture purposes. The grapes belonged to *V. vinifera* L. cv. Aglianico, an autochthonous Campania Region cultivar. Vineyards were grass-covered and managed without manure treatments, under organic farming. In the days of the grape harvest and in the five days preceding the harvest, from 0 to 0.2 mm of rain a day were registered from the Montemarano Agro-meteorological Station (Assessorato Agricoltura, 2020). Grapes were collected within a radius of 2 m from the soil sampling point, in triplicate, on 6 plants at a point. Berries were collected with pedicel, randomly from different parts (upper-shoulders, middle, and lower-tip sections) of the bunch, at different heights from the soil, for a total of 250 berries at a point. Only undamaged and sound berries were sampled, cutting the pedicel just upon the base. Fresh samples (less than 4 h from the collection) were processed. Berry weight was measured on 100 berries. All grape analyses were performed according to the OIV methods (OIV, 2021). Fifty berries were pressed (3 bar) to obtain the juice for: 1) total soluble solids (TSS) measurement by digital refractometer Hanna Instrument (Dongare et al., 2015), and data were expressed as Brix degree (°Bx), 2) total acidity determination by 0.1 M NaOH and titration with bromothymol blue as indicator, and comparison with an end-point color standard, 3) grape pH by potentiometric determination. Grape samples to use for element profile and phenolic compounds analyses were washed with Milli-Q water, blotted with clean paper, and frozen (−20 °C).

2.3.2. Element profile of seeds, pulp, and skin

Fifty frozen berries (−20 °C) were weighed, manually peeled, and carefully separated into 3 grape tissues: seed, pulp, and skin. Seeds and skin, separately, were manually cleaned for pulp removal, blotted with clean paper, weighed, and homogenized after the addition of an equal weight of Milli-Q water by Ultra-Turrax T25 high-speed homogenizer. A micro blender with plastic blades was used to homogenize the pulp. The pulp weight was obtained by subtracting the weight of seeds and skin from the total berry weight. Knowing the weight of each tissue in 50 berries and the weight of the 50 berries, the weight (kg) of each grape tissue in 1 kg of whole grapes was calculated. Then, the fraction of tissue contributing to 1 kg of grape (i.e., f_s = seed fraction, f_p = pulp fraction, f_{sk} = skin fraction) was calculated: f_s = seeds weight (kg) / 1 kg of grape, and in the same way for f_p and f_{sk}. This calculation was performed for each analysed grape sample. The high-performance microwave (HPMW) acid digestion was applied for the grape tissue digestion (Catarino et al., 2010). The HPMW is the protocol offering higher performance for organic matter destruction in samples with high sugar content (Catarino et al., 2010; Gajek et al., 2021). Homogenized samples of seeds (1.0 g fresh weight, FW), pulp (3.0 g FW), and skin (2.0 g FW) were acid digested with 65 % HNO_3 using a microwave system (Milestone, Start D model, Shelton, USA) equipped with 10 positions (1 position is supplied by pressure and temperature control probe) of 50 ml PTFE vessels. For the digestion, 6 ml of HNO_3 and 2 ml of Milli-Q water were added to the samples and kept for 1 h at room temperature under a chemical hood. This is a modified procedure of Milićević et al. (Milićević et al., 2017). The accuracy of the complete digestion of the grape tissue was verified using TEA LEAVES Polish Certified Reference Material (ICHTJ, 2017). In a batch of 8 samples, 1 blank test, and 1 sample of certified reference material (0.3 g) were digested using the same procedure applied to the grape samples. The digestion power ramp to 1000 W was 10–15-15 min at 100–150-200 °C, respectively. After cooling, the digested solutions were completed to a 25 ml final volume with Milli-Q water. Samples for Ca, K, Mg, P, S elements determination were diluted 10-fold with Milli-Q water, while those for B, Cu, Fe, Li, Mn, Na, Si, Sr and Zn were diluted 2-fold. The multi-element analysis was performed with ICP-OES (iCAP 7400 Analyzer - Thermo Fisher Scientific - USA). Element concentrations measured in the digested solutions of seeds, pulp, and skin ($C'x_{s,p,sk}$) were referred to 1 kg of each tissue ($Cx_{s,\ p,\ sk}$), as follows:

$$Cx_{s,p,sk}\left(mg\ kg^{-1}\right) = \frac{C'x_{s,p,sk} \times DF \times final\ volume}{m_{s,p,sk}} \quad (1)$$

$C'x_{s,p,sk}$ = element (x = B, Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Si, Sr, Zn, Li) concentration (mg L^{-1}) measured by ICP-OES in seeds, pulp and skin, DF = dilution factor of elements, final volume = 25 ml, $m_{s,p,sk}$ = mass (g) of the digested sample.

Blank samples were analysed, and both LODm and LOQm were calculated following the same procedure applied for the bioavailable element content (section 2.2.2). A recovery test using the reference material allowed for the estimation of the accuracy of the digestion procedure.

The elemental content of 1 kg of grape berries (Cx_{berry}), also defined as the grape total element profile, was calculated as follows:

$$Cx_{berry}\ \left(mg\ kg^{-1}\right) = (Cx_s \times f_s) + \left(Cx_p \times f_p\right) + (Cx_{sk} \times f_{sk}) \quad (2)$$

Cx_s, Cx_p, Cx_{sk} = concentration of elements in 1 kg of each tissue (mg kg^{-1}), as calculated by Eq. 1; f_s, f_p, f_{sk} = fraction of seeds (f_s), pulp (f_p), and skin (f_{sk}) (dimensionless) in 1 kg of grape, as calculated at the beginning of this section.

2.3.3. WLJ preparation and analyses

Polyphenols were extracted from frozen samples of berries (−20 °C) in duplicate. The "final extraction protocol" proposed by Jensen et al. (2007) was applied as an extraction method to analyse the polyphenols in grapes. The extract was named wine-like-juice (WLJ), since the use of ethanol as the most relevant extraction solvent mimics the events taking place during winemaking (Jensen et al., 2007). That proposed by Jensen is an optimized extraction protocol obtained with 5 min of solvent contact time using 50 % *v/v* aqueous ethanol with 0.1 M HCl (acidic ethanol) at 40 °C and a 1:1 *w/v* grape homogenate: solvent ratio, followed by acid neutralization with 5 M NaOH and sample clarification. In detail: for each sampling point of the vineyard, 100 g of grapes were destemmed, thawed, and homogenized for 2 min with an Ultra-Turrax T25 high-speed homogenizer. Fifteen g of homogenate was weighed in a 50 ml plastic test tube and mixed with 15 ml acidic ethanol, which had been preheated to 60 °C. The mixture was sealed and stirred with a magnetic bar at 40 °C. After 5 min, 0.3 ml of 5 M NaOH was slowly added while stirring for 1 min to neutralize the HCl. Samples were centrifuged for 10 min at 15,000 *g* and filtered through a Whatman grade 4 cellulose filter.

Separately, 50 g homogenate was weighed (m_{h50} in g), centrifuged as above, and the supernatant (i.e., the juice) weighed (m_{j50} in g). Twenty-five ml of the supernatant was poured into a calibrated cylinder and weighed (m_{j25} in g) to estimate the juice density (ρ_j), as follows: ρ_j (g ml^{-1}) = m_{j25} / 25. The volume (V_{j50}) of the juice extracted from the 50 g homogenate was calculated as follows: V_{j50} (ml) = m_{j50} / ρ_j. Then, the exact volume of the juice (V_{j15} in ml), corresponding to 15 g homogenate (m_{h15} = 15 g) used for the extraction of polyphenols, was calculated: $V_{j15} = m_{h15} \times V_{j50} / m_{h50}$. All weights were recorded precisely (3 decimals) as they are used in the calculations of both phenolic content and element concentration in the WLJs.

The main classes of phenolic compounds, including bovine serum albumin -BSA- reactive tannins, total anthocyanins, bound anthocyanins, and total phenols (also named IRPs - iron reactive phenolics) were analysed in the WLJ by an adapted procedure of the Harbertson assay (Harbertson et al., 2002, 2003) for the microplate platform (Heredia et al., 2006). The method is based on the absorbance measurement at 520 nm of the solutions resulting from the use of the BSA to precipitate polymeric forms, and the decolorization of monomeric forms with sulphur dioxide. Catechin (+) standard curve was prepared using a set of catechin (+) dilutions to cover a range of 0–300 mg L^{-1} catechin (0, 50, 100, 150, 200, 250, 300 mg L^{-1}). Spectrophotometric measures were performed with a Thermo Fisher Varioskan Flash spectrophotometer. The content of total anthocyanins, short and large polymeric pigments (by the sum of the short and large polymeric pigments is obtained the bound anthocyanins content), tannins, and total phenols-IRPs in the WLJ was calculated by applying formulae reported in the Heredia assay (Heredia et al., 2006). The tannins and IRPs content were expressed as catechin equivalent (CE). The total and bound anthocyanins were expressed in malvidin-3-glucoside (ME) by applying the generic extinction coefficient (ε = 0.0102), as reported by Jensen et al. (2007) and Heredia et al. (2006).

The content (C'ph) of each phenolic compound (i.e., bound and total anthocyanins, tannins, and IRPs, in mg L^{-1}) of the WLJ was referred (Eq. 3) to 1 kg of homogenate (Cph), which corresponds to 1 kg of grapes, as follows:

$$Cph\ \left(mg\ kg^{-1}\right) = \frac{C'ph \times \left(V_{ext} + V_{j15}\right)}{m_{h15}} \quad (3)$$

C'ph = content of each phenolic compound (mg L^{-1}), including the tannins, IRPs, bound and total anthocyanins, as measured by Heredia assay in the WLJ; V_{ext} = volume of the extractant solutions (ml) made by 15 ml acidic aqueous ethanol and 0.3 ml 5 M NaOH; V_{j15} = the calculated juice volume (ml) extracted by 15 g of homogenate; m_{h15} = mass of homogenate (g) used for the extraction, corresponding to 15 g of grapes.

Then, the Glories procedure (Glories, 1984) was used for color intensity (CI) and hue determinations. Samples of WLJ were diluted 1:10 (*v/v*) with a solution made of 12 % *v/v* ethanol with 5 g L^{-1} tartaric acid adjusted to pH 3.3 with 5 M NaOH. The absorbances at 420, 520, 620, and 700 nm of the diluted samples were measured in 10-mm quartz cuvettes by a Perkin Elmer UV/VIS Lambda 365 spectrophotometer. Color intensity (CI) was calculated by the sum of the absorbances at 420 (yellow), 520 (red), and 620 nm (blue), while the hue was obtained by the ratio of 420/520 absorbances. Data of the absorbance at 700 nm were used to check the turbidity of the samples.

After that, the elemental composition of the WLJ was analysed for inferences on the potential transfer of elements from the grapes to wines. The element content of the WLJ was measured after sample acid digestion with 65 % HNO_3, in the same HPMW system and at the same power ramp used for the grape digestion. The HPMW is recommended for sample mineralization before multielemental analysis by ICP, which is the procedure adopted by the International Organization of Vine and Wine (OIV) for wines containing more than 100 g L^{-1} of sugar (OIV, 2023). We applied a modified version of the mineralization method for grape musts and wine analyses proposed by Catarino et al. (Catarino et al., 2010). Briefly, 2 ml of WLJ sample was added with 4 ml of 65 % HNO_3 and 4 ml of Milli-Q water, kept for 1 h at room temperature under a chemical hood, and then digested. After cooling, digested mixtures were completed to a 20 ml final volume with Milli-Q water. No further dilution was applied to the samples. Boron, Ca, Cu, Fe, K, Mg, Mn, Na, P, Si, Sr, Zn, Li were measured by ICP-OES analyzer (iCAP 7400 Analyzer - Thermo Fisher Scientific - USA). The obtained concentrations were multiplied by 10, considering that the 2 ml of the WLJ sample was completed to 20 ml as the final volume (1:10 *v/v*) after acid digestion. Blank samples were included in each procedure, and both LODm and LOQm were calculated following the procedure applied for the bioavailable element content (section 2.2.2). A recovery test to evaluate the accuracy of the extraction procedure was performed using spike solutions.

The element (x) concentration in the WLJ (WLJ x), as produced by 1 kg of grapes (mg kg^{-1}), was calculated (Eq. 4) as follows:

$$WLJ\ x\ \left(mg\ kg^{-1}\right) = \frac{C'x \times \left(V_{ext} + V_{j15}\right)}{m_{h15}} \quad (4)$$

C'x = concentration (mg L^{-1}) of elements (x = B, Ca, Cu, Fe, K, Mg, Mn, Na, P, Si, Sr, Zn, Li) measured by the ICP-OES analyzer; V_{ext} = volume (ml) of the extractant solution, which is made of 15 ml acidic aqueous ethanol and 0.3 ml 5 M NaOH; V_{j15} = the calculated juice volume (ml) extracted by the homogenate; m_{h15} = mass (g) of

homogenate used for the extraction.

2.4. Transfer coefficient (TC), bioconcentration factor (BF)

To calculate the transfer coefficient (TC) of elements (x) from the grape berries to the WLJ, Eq. 5 was applied:

$$TCx = \frac{WLJx}{Cx_{berry}} \quad (5)$$

WLJx = concentration (mg kg^{-1}) of elements (x = B, Ca, Cu, Fe, K, Li, Mg, Mn, Na, P, Si, Sr, Zn) in the WLJ due to 1 kg of grapes, as calculated with the Eq. 4; Cx_{berry} = concentration (mg kg^{-1}) of elements (x) in 1 kg of grape berries (as calculated with the Eq. 2). To determine elemental transfer from soil to grape berry tissues, the bioconcentration factor (BF) was calculated for the different elements (x), as follows:

$$BF\ x_{s,p,sk} = \frac{x_{s,p,sk}}{NH_4OAc\ soil\ bioavailable\ element\ x} \quad (6)$$

$x_{s,p,sk}$ = concentration of elements (x = B, Ca, Cu, Fe, K, Li, Mg, Mn, Na, P, S, Si, Sr, Zn) in the seeds, pulp or skin (mg kg^{-1}); NH_4OAc soil bioavailable element x = concentration of the bioavailable elements (x) (mg kg^{-1}) extracted with NH_4OAc solution. To visualize the calculated ratios, data were logarithmically transformed and plotted.

2.5. Statistical analysis

IBM SPSS Statistics for Windows (IBM Corp. Released 2020, Version 27.0. Armonk, NY, USA: IBM Corp) was used for basic statistics and correlation studies. The normality and homogeneity of the variances were assessed by Shapiro-Wilk's test (Shapiro & Wilk, 1965) and Levene's test (Levene, 1960), respectively. The nonparametric Spearman's rank correlation coefficient was applied to determine relationships between variables. Each correlation coefficient was calculated considering all the replicates of measurements, and only significance with *p*-values <0.05 was evaluated, according to Bonferroni's correction (Bonferroni, 1936) to counteract multiple comparison problems. The statistically significant differences among the groups of each independent variable (sites and depths, fruit tissues) were assessed on the continuous dependent variables (total and bioavailable soil element composition, soil chemical and physical properties, element profiles of grapes and WLJs, BFs, grape characteristics and WLJ phenolic content) by the nonparametric Kruskal-Wallis analysis of variance (Kruskal & Wallis, 1952) by ranks followed, in case of rejection of the null-hypothesis, by Dunn's test with Bonferroni's multiple comparison adjustments (Dunn, 1961). After data standardization, a Principal Component Analysis (PCA) was applied to the whole dataset of soil properties, BFs, grape, and WLJ characteristics, to explore their relation to the sites and depths.

3. Results and discussion

3.1. Soil chemical and physical properties, total and bioavailable element content

Data of the soil chemical and physical properties are reported in Table 2, and trends across the sites are shown in Fig. S1 (Appendix C. Supplementary material). Soil pH showed moderately alkaline in the topsoils (from 8.26 to 8.45) but increased to strongly alkaline with depth (8.47–8.59), consistently with total carbonates, which showed moderate contents (from 94 to 214 g kg^{-1}) increasing with depth (Table 2). The highest pH values were found in TA-O mineral and bottom soils, and in TA-Y the bottom soil showed the highest pH variability. The soil EC was generally low in all soil horizons (from 141 to 194 μS cm^{-1}) but showed a sharp increase in the TA-Y bottom soil (EC = 280 μS). Nevertheless, none of the measured EC values indicated any salinity problems in the soil. The available phosphorus content was generally low in the topsoil (from 14.3 to 31.0 mg kg^{-1}), and due to the high soil pH, phosphorus was poorly available for plants. The organic carbon content (OC) was generally low both in the topsoil (from 9.89 to 11.32 g kg^{-1}) and the mineral soil horizon (from 4.66 to 7.03 g kg^{-1}), in relationship with the clayey family texture (clay content from 428 to 509 g kg^{-1}). However, the OC content was very similar among the sites, and, as expected, regularly decreased with depth.

Rather homogeneous and moderately high was the cation exchange capacity (CEC) (from 21.57 to 28.92 $cmol^{(+)}$ kg^{-1}) with exchangeable Ca (Ca_{ex}) as the prevalent cation, followed by Mg_{ex} (from 1.72 to 4.22 $cmol^{(+)}$ kg^{-1}), K_{ex} (from 0.88 to 3.66 $cmol^{(+)}$ kg^{-1}), and Na_{ex} (from 0.34 to 1.19 $cmol^{(+)}$ kg^{-1}); the Mg_{ex}/K_{ex} ratio was generally balanced (ratio from 1.3 to 4.5). Dunn's test revealed several differences among the sites (Table 2). Of particular note were the higher K_{ex} values in the TA-O vineyard compared to all the other sites, and the nearly twofold higher Na_{ex} content in the bottom soil (70–100 cm deep) of the TA-Y vineyard compared to the other sites. Furthermore, the ESP was generally increasing with depth (from 1.20 to 1.69 % in the topsoil; from 1.59 to 4.05 %), except for TA-O, where the ESP was higher starting from the topsoil (2.79 %). However, all the values did not fulfil the requirements of the sodic qualifier provided by the WRB soil classification, i.e., Na plus Mg ≥ 15 % and Na ≥ 6 %, both on the exchange complex (IUSS Working Group WRB, 2022). Despite the described differences, highly homogeneous trends of soil properties were identified among the sites (Fig. S1, provided in Appendix C. Supplementary material).

The mean of the soil total element content, including Al, As, Ca, Cr, Cu, Fe, K, Mn, Nb, Pb, Rb, Si, Sr, Th, Ti, V, Y, Zn, and Zr, according to the investigated vineyards, is reported in Table S1, and the validation parameters of the element determinations are shown in Table S2 (provided in Appendix D. Supplementary material). The trends of the soil geochemical composition allowed assessment of a whole homogeneous soil parent material within the TA sites (Fig. S2). Some differences were observed in the TA-O vineyard, where the Al, Mn, Si, Cr, and V content was lower than at the other sites. These differences were significant at the Dunn's test ($p < 0.05$) for Al and V only in the topsoil, while for Si and Cr the difference was significant ($p < 0.05$) for all the soil depths (Table S1). Moreover, several differences were found among the sites for Mn and Fe, suggesting possible variation in local soil redox conditions due to seasonal fluctuations in the water table, which produced Fe—Mn oxide precipitation (IUSS Working Group WRB, 2022). Worth noting, a wide range of variability of the Ca content for all the analysed soils was found, very likely due to the presence of secondary carbonate concretions formed by dissolution and precipitation processes occurring at different extents within the vineyard soils.

The soil bioavailable element content depends on the form in which the element occurs in the soil (i.e., silicates, oxides, organic complexes, etc) and allows insights into the availability for plant nutrition. Therefore, the bioavailable content represents a better proxy to relate soil and grape composition than the total content. The mean of the soil bioavailable element concentrations is reported in Table S3, and the validation parameters of the element determinations are shown in Table S4 (provided in Appendix D. Supplementary material). In terms of percentage of the total content, the bioavailability of the analysed elements was in the order: Ca (10–18 %) > Sr (7.7–19 %) > K (1.9–8.3 %) > Cu (1.3–2.4 %) > Mn (0.4 –1.5 %) > Zn (0.2–0.6 %) > Si (0.018–0.033 %) > Fe (2.0×10^{-4}–1.4×10^{-3} %). Overall, highly homogeneous trends were identified across the sites for the bioavailable element content (Fig. S3, Appendix C. Supplementary material), except for the bottom soil of TA-Y, which showed higher content of bioavailable B, Mg, K, and Na compared with the same horizon in the other vineyards. The observed increase of Na, Mg, and K was consistent with the increase found for Na_{ex}, Mg_{ex}, and K_{ex} (Table 2). Nevertheless, according to the Dunn's test, the differences were significant only for the bioavailable K, and the

Table 2
Chemical and physical properties of the vineyard soils from the Taurasi (TA) DOCG terroir. Uppercase letters (A, B, C) were used to compare the mean values of the soil properties among horizons within the same site (column 1), lowercase letters (a,b,c) for comparison among sites for the same horizon (column 2), according to Dunn's test ($p < 0.05$). The number of cases (n) analysed for each vineyard is 12 at each depth (total $n = 180$ across the 5 vineyards). NS in column 1 and ns in column 2 define no significant differences, according to Kruskal-Wallis analysis of variance by ranks.

Soil properties/Sites		TA-A				TA-B				TA-S				TA-O				TA-Y			
		Mean	±SD	1	2	Mean	±SD	1	2	Mean	±SD	1	2	Mean	±SD	1	2	Mean	±SD	1	2
pH (H_20)	0–30	8.30	0.09	NS	ab	8.32	0.16	NS	ab	8.26	0.10	NS	b	8.45	0.08	NS	a	8.31	0.22	NS	ab
	30–70	8.35	0.09	NS	ns	8.40	0.18	NS	ns	8.40	0.14	NS	ns	8.59	0.17	NS	ns	8.39	0.19	NS	ns
	70–100	8.39	0.08	NS	ns	8.43	0.16	NS	ns	8.47	0.15	NS	ns	8.68	0.09	NS	ns	8.59	0.33	NS	ns
EC (mS/cm)	0–30	177.61	11.81	NS	ns	159.23	8.59	NS	ns	171.66	5.91	B	ns	189.42	7.80	NS	ns	193.74	8.86	NS	ns
	30–70	171.73	8.43	NS	ab	141.45	25.82	NS	b	157.94	8.59	B	ab	184.63	10.58	NS	a	189.75	22.01	NS	a
	70–100	170.70	8.84	NS	bc	142.81	32.55	NS	c	162.48	26.82	A	bc	187.03	9.19	NS	b	279.63	93.50	NS	a
Total carbonates (g kg^{-1})	0–30	93.8	39.5	NS	ns	127.3	50.0	NS	ns	126.9	83.4	NS	ns	170.1	61.9	NS	ns	157.5	70.4	NS	ns
	30–70	94.7	49.7	NS	ns	142.9	68.5	NS	ns	184.6	143.6	NS	ns	162.0	100.0	NS	ns	158.2	80.5	NS	ns
	70–100	142.6	62.9	NS	ns	175.5	84.8	NS	ns	214.3	182.1	NS	ns	166.0	79.9	NS	ns	183.3	98.1	NS	ns
OC (g kg^{-1})	0–30	10.1	1.3	A	ns	11.3	2.5	A	ns	10.8	3.7	A	ns	10.5	2.2	A	ns	9.9	1.6	A	ns
	30–70	7.0	1.8	B	ns	5.0	2.4	BC	ns	4.7	3.0	B	ns	5.4	1.9	B	ns	6.4	2.5	BC	ns
	70–100	3.8	2.6	C	ns	1.8	0.6	C	ns	2.2	0.7	C	ns	3.5	1.5	B	ns	2.7	0.4	C	ns
sand (g kg^{-1})	0–30	288	24	NS	a	309	36	NS	a	238	43	NS	ab	174	74	NS	ab	148	79	NS	b
	30–70	293	36	NS	a	277	57	NS	a	203	74	NS	ab	186	41	NS	ab	149	94	NS	b
	70–100	273	31	NS	ns	255	105	NS	ns	203	87	NS	ns	180	55	NS	ns	157	148	NS	ns
silt (g kg^{-1})	0–30	240	44	NS	b	261	38	NS	ab	253	43	NS	ab	399	99	NS	a	356	79	NS	a
	30–70	233	57	NS	b	266	86	NS	ab	300	62	NS	ab	363	72	NS	a	349	75	NS	a
	70–100	268	40	NS	ns	306	82	NS	ns	304	83	NS	ns	381	83	NS	ns	362	97	NS	ns
clay (g kg^{-1})	0–30	473	45	NS	ns	430	66	NS	ns	509	40	NS	ns	428	47	NS	ns	496	38	NS	ns
	30–70	474	49	NS	ns	457	86	NS	ns	497	38	NS	ns	451	59	NS	ns	502	53	NS	ns
	70–100	458	52	NS	ns	440	115	NS	ns	493	41	NS	ns	439	49	NS	ns	481	85	NS	ns
Available P (mg kg^{-1})	0–30	13.53	5.83	NS	ns	6.26	2.17	NS	ns	7.34	4.21	NS	ns	6.81	2.10	A	ns	9.45	4.72	NS	ns
	30–70	7.85	3.40	NS	ns	1.94	0.77	NS	ns	5.42	7.19	NS	ns	2.86	0.86	B	ns	6.69	5.02	NS	ns
	70–100	6.25	3.83	NS	ns	1.09	0.92	NS	ns	3.16	3.92	NS	ns	1.83	0.71	C	ns	2.42	1.45	NS	ns
CEC (cmol $^{(+)}$ kg^{-1})	0–30	27.96	3.34	NS	ns	25.43	3.76	NS	ns	28.92	2.03	NS	ns	23.22	4.14	NS	ns	26.72	4.00	NS	ns
	30–70	27.39	3.49	NS	ns	24.38	4.81	NS	ns	26.98	3.66	NS	ns	21.57	5.35	NS	ns	25.80	4.19	NS	ns
	70–100	25.99	3.04	NS	ns	23.23	5.55	NS	ns	25.83	3.74	NS	ns	22.39	4.59	NS	ns	25.68	3.97	NS	ns
Ca_{ex} (cmol $^{(+)}$ kg^{-1})	0–30	23.64	3.16	NS	a	22.18	2.93	NS	ab	25.02	2.30	NS	a	16.08	4.00	NS	b	22.27	4.16	NS	ab
	30–70	23.40	3.31	NS	a	21.14	3.67	NS	ab	22.85	3.83	NS	ab	14.98	4.58	NS	b	20.78	3.84	NS	ab
	70–100	21.94	2.68	NS	ns	19.56	4.22	NS	ns	20.85	3.48	NS	ns	16.18	4.51	NS	ns	19.25	2.75	NS	ns
K_{ex} (cmol $^{(+)}$ kg^{-1})	0–30	1.57	0.24	NS	b	1.14	0.19	NS	c	1.10	0.11	NS	c	3.10	0.90	NS	a	1.52	0.30	NS	b
	30–70	1.28	0.23	NS	b	0.90	0.23	NS	bc	0.88	0.17	NS	c	3.66	1.42	NS	a	1.50	0.37	NS	b
	70–100	1.18	0.16	NS	b	0.91	0.33	NS	bc	0.88	0.20	NS	bc	3.38	1.14	NS	a	1.14	0.45	NS	b
Mg_{ex} (cmol $^{(+)}$ kg^{-1})	0–30	2.29	0.63	NS	ns	1.72	0.84	NS	ns	2.45	0.52	NS	ns	2.44	0.62	NS	ns	2.60	1.59	NS	ns
	30–70	2.17	0.46	NS	ns	1.91	1.24	NS	ns	2.88	0.69	NS	ns	1.87	0.70	NS	ns	3.00	1.58	NS	ns
	70–100	2.26	0.58	NS	ns	2.32	1.75	NS	ns	3.69	1.16	NS	ns	2.16	0.56	NS	ns	4.22	2.19	NS	ns
Na_{ex} (cmol $^{(+)}$ kg^{-1})	0–30	0.47	0.05	NS	ns	0.39	0.03	NS	ns	0.35	0.04	A	ns	1.19	1.41	NS	ns	0.34	0.11	NS	ns
	30–70	0.54	0.06	NS	ns	0.42	0.07	NS	ns	0.36	0.05	A	ns	0.58	0.28	NS	ns	0.52	0.27	NS	ns
	70–100	0.61	0.15	NS	b	0.44	0.10	NS	bc	0.41	0.08	B	bc	0.67	0.33	NS	b	1.07	0.60	NS	a
ESP %	0–30	1.69	0.23	NS	ns	1.55	0.27	NS	ns	1.20	0.15	NS	ns	2.79	1.36	NS	ns	1.30	0.43	NS	ns
	30–70	2.00	0.32	NS	ns	1.77	0.31	NS	ns	1.37	0.26	NS	ns	2.69	1.22	NS	ns	2.01	0.99	NS	ns
	70–100	2.37	0.61	NS	ab	1.96	0.52	NS	ab	1.59	0.28	NS	b	3.00	1.20	NS	a	4.05	2.14	NS	a

Legend: pH (H_2O): pH in water; EC = electrical conductivity; OC = organic carbon; available P = available phosphorus; CEC = cation exchange capacity; Ca_{ex}, K_{ex}, Mg_{ex}, Na_{ex} = exchangeable Ca, K, Mg, and Na; ESP = exchangeable sodium percentage.

Table 3
Enological characteristics of the Aglianico grapes, color intensity, hue, bound and total anthocyanins, tannins and total phenols of the wine-like juice obtained following the Jensen procedure, from all the sites of the Taurasi DOCG terroir, were reported. Lowercase letters (a,b,c) were used to compare the mean ranks of the distributions according to Dunn's test ($p < 0.05$). Total acidity is expressed in grams of tartaric acid per liter (g L^{-1}). Bound and total anthocyanins were expressed as malvidin equivalent (ME), while tannins and total phenols -IRPS as catechin equivalent (CE).

Sites		TA-A			TA-B			TA-S			TA-O			TA-Y		
		Mean	±SD		Mean	±SD		Mean	±SD		Mean	±SD		Mean	±SD	
grape characteristics																
Total soluble solids – TSS	°Bx	22.4	1.0	a	21.6	1.2	b	23.2	1.2	a	23.0	1.2	a	22.3	0.9	ab
pH		3.2	0.1	b	2.9	0.1	d	3.0	0.1	c	3.3	0.1	a	3.3	0.1	a
Total acidity	tartaric acid g L^{-1}	8.2	0.5	b	10.0	0.6	a	9.9	1.2	a	6.8	1.3	c	6.4	1.0	c
Weight of 100 berries	g	199.1	5.4	b	212.6	14.9	a	185.7	15.7	b	177.9	11.8	b	182.9	14.8	b
wine-like juice characteristics																
Color intensity		11.7	1.7	c	8.9	1.8	d	16.4	1.8	a	13.1	1.6	b	14.0	1.5	b
Hue		0.5	0.0	bc	0.5	0.1	ab	0.4	0.0	c	0.4	0.0	d	0.5	0.0	a
Bound anthocyanins	mg kg^{-1} ME	98.8	8.2	b	73.6	7.2	c	93.4	8.3	b	125.1	14.3	a	132.8	4.0	a
	mg L^{-1} ME	66.0	5.1	b	49.3	4.9	c	62.4	5.7	b	100.3	17.0	a	88.9	2.3	a
Total anthocyanins	mg kg^{-1} ME	564.4	94.6	b	415.0	114.1	c	896.9	76.9	a	740.0	143.1	a	862.0	30.4	a
	mg L^{-1} ME	377.6	69.9	b	278.0	83.3	c	599.8	52.5	a	374.5	112.9	a	577.1	19.2	a
Tannins	mg kg^{-1} CE	797.2	92.5	b	887.4	48.8	b	834.8	71.8	b	974.3	208.0	ab	1078.8	70.8	a
	mg L^{-1} CE	533.3	67.4	b	594.5	32.7	b	555.5	44.6	b	740.0	104.1	ab	722.3	49.1	a
Total phenols- IRPs	mg kg^{-1} CE	1555.3	91.8	c	2182.0	95.0	b	2264.1	142.8	b	2132.0	470.5	ab	2805.8	62.1	a
	mg L^{-1} CE	1040.4	65.3	c	1461.8	51.4	b	1512.9	87.8	b	1761.7	311.3	ab	1878.7	15.7	a

exchangeable Na and K.

3.2. Enological characteristics and element profile of the grape berries

Results of enological characteristics are reported in Table 3. Ripeness levels at harvest (TSS ranging from 21.6 and 23.2°Bx) of the Taurasi grapes analysed in this work were consistent with the Campania regulation for the Taurasi wine production area (Disciplinare di produzione dei vini a DOCG "Taurasi", 1993, reported in Appendix B. Supplementary material), which provides that the Aglianico grapes must ensure the minimum natural alcoholic strength by volume of 12 %, which in terms of TSS corresponds to approximately 20°Bx. Therefore, the analysed grapes can all be considered technologically ripe. The most relevant difference among the sites was the significantly highest pH values of TA-O and TA-Y grapes ($p < 0.05$), associated with the lowest total acidity. The Spearman correlation coefficient calculated for the grape enological characteristics (Fig. S4) allowed the identification of a significant correlation ($p < 0.05$) between berry weight and pH values. The berry size (here considered in terms of weight) is important in determining fruit and wine quality. It is generally accepted that relatively small berries give excellent wine quality (Chen et al., 2018). The pH is considered the most important measure of juice and wine acidity, since it plays several important roles, including the control of malolactic fermentation (Rankine et al., 1970), the extent of K bitartrate precipitation (Mpelasoka et al., 2003). Too acidic grapes (value of total acidity higher than 6 g L^{-1} expressed as tartaric acid) are generally not preferred for the Taurasi wines because of the astringent tannins (Picariello et al., 2019). This study showed that a low pH negatively affects the sensory properties of tannins due to stronger binding between tannins and salivary proteins when tasting. This implies that the lower the berry weight and the slightly higher the pH are quality characteristics for the investigated grape cultivar and terroir.

The element profile of the grape tissues is reported in Table S5, and the validation parameters are reported in Tables S6 (Appendix D. Supplementary material). Significant differences ($p < 0.05$) were identified between the seeds and both the pulp and skin for many elements, including Ca, Fe, Mg, Mn, Na, P, S, Sr, and Zn (see the element concentration in kg of tissue in Table S5). The elements in the pulp were found in the order: K > P > S > Ca > Mg > Na > Si > B > Fe > Cu > Zn > Sr > Mn > Li. This order was very similar in the skin, except for Cu, which was higher than Fe, and for Sr, higher than Zn. Seeds were the main sink for Ca, Fe, Mg, Mn, Na, P, S, Sr, and Zn, while Cu was mostly accumulated in both the skin and seeds, and B, K, and Si in the skin (Table S5). Measured data are strongly consistent with those found by Rogiers et al. for the grapes of the Shiraz red wine (Rogiers et al., 2006), except for Fe, which is found primarily accumulated in the pulp and skin in the Shiraz grapes. Bertoldi et al. (2011) found the seeds as the main sink for Ca, Mn, P, and Zn in the grapes of Chardonnay, and the skin as the main sink for B. On the contrary, K, Mg, and Na were mostly accumulated in the pulp of Chardonnay. Iron was not significantly enriched in the seeds of all vineyards. Differences in element patterns of grape tissues can be related to the different cultivars and environmental conditions. Indeed, for elements with variable or conditional phloem mobility (including B, Cu, Fe, and Zn), evidence was found of their dependence on plant species, environmental influences, plant tissue, and growth stage (Rogiers et al., 2006; Welch & Rengel, 1999). It is worth noting that Fe is mostly accumulated in the seeds of the Taurasi grapes, as well as Mn, Cu, and Zn. These elements are known to influence several processes in wines and cause wine faults, negatively affecting wine's taste and aroma, aging, and color. Likewise for Na, which is mainly concentrated in the seeds. Wine providing high Na content has been described as salty, flat, dull, etc. These findings and wine producers' awareness of the distribution of these elements among the grape tissues give the possibility to better tune winemaking processes and reduce possible undesirable wine traits.

Considering the maximum acceptable limits identified by OIV (OIV, 2024, reported in Appendix B. Supplementary material) for wines, only Cu values (0.40 mg kg^{-1} in grape seeds, 1.76 mg kg^{-1} in pulp, and 1.29 mg kg^{-1} in the skin) (Table S5) may represent a potential risk to obtain wines exceeding the provided limit (1 mg L^{-1}). However, given that the

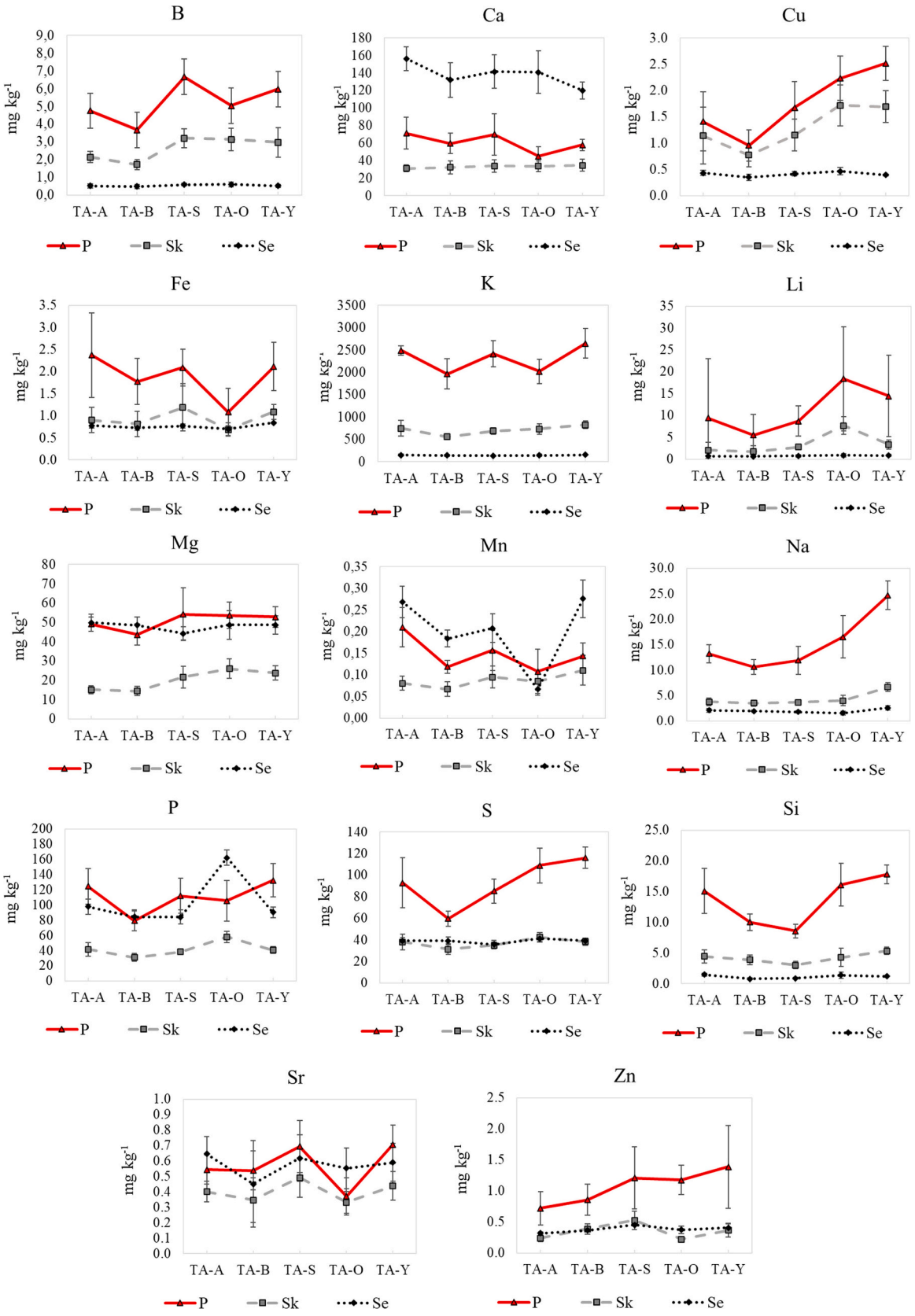

Fig. 2. Element profile, including nutrients (Ca, K, Mg, P, S, B, Cu, Fe, Mn, Zn), beneficial (Na, Si) and other elements (Li, Sr) content, of the five vineyards from the Taurasi terroir.

concentration of Cu in wine is lower than in grapes due to adsorption on yeast lees during fermentation, the Cu content found in the TA grapes is not a cause for concern. Examining the variability of the element profile across the sites (Fig. 2), similar trends were evident for the skin and pulp for almost all element contents, except for P. Worthy of note were the significantly higher ($p < 0.05$) contents of Cu and Na in the pulp of TA-Y compared with TA-B, as well as of Si in the pulp of TA-O and TA-Y than TA-B and TA-S (Dunn's test in Table S5).

3.3. Phenolic compounds, WLJ element profile, and relationship with the grape composition

Application of the Jensen protocol was tested in place of the wine preparation to obtain a more reproducible dataset and less time-consuming replicates of a wine "proxy" from the Taurasi terroir, for correlations with grape composition and soil properties. Enological characteristics and phenolic compounds content of the WLJ were reported in Table 3. Values of color intensity (CI) were on average 13, in a range from 9 at TA-B to 16 at TA-S, while the mean hue was 0.5. Evaluating the phenolic compounds, the highest values of total anthocyanins (862 mg kg^{-1} ME), bound anthocyanins (133 mg kg^{-1} ME), tannins (1079 mg kg^{-1} CE), and total phenols-IRPs (2805 mg kg^{-1} CE) were found for the TA-Y vineyard. On the contrary, the lowest values of total (415 mg kg^{-1} ME) and bound anthocyanins (73.57 mg kg^{-1} ME) were measured for TA-B, while for the tannins and total phenols-IRPs the lowest values were found for TA-A (798 and 1555 mg kg^{-1} CE, respectively). Examining the enological characteristics reported by Muccillo et al. (2014) for various red wines produced from different grape varieties of the Campania region, there is a high degree of similarity between our WLJ and the analysed Aglianico di Taurasi wine concerning CI, which ranges from 9 to 16 in our WLJ and is 14 in the Aglianico di Taurasi wines analysed by Muccillo et al. (2014). The same is true for the total anthocyanins, ranging from 277 to 600 mg L^{-1} ME in the WLJ, and from 534 to 559 mg L^{-1} ME in the wines reported by Muccillo et al. (2014). On the contrary, the tannin content of the WLJ was strongly underestimated (533–740 mg L^{-1} CE) compared to the wines analysed by Muccillo et al. (2014) (3730 mg L^{-1} CE). This is consistent with that known in general about methods for polyphenols extraction from grapes, including the method proposed by Jensen et al. (2007, reported in Appendix B. Supplementary material) used in this study, namely, that anthocyanins are easily extracted from grape skins with different solvents (acidic methanol, acidic ethanol, or acetone/water) (Macheix et al., 2018), while extraction of phenols from grape seeds during the procedures is more challenging. This makes us aware that the WLJ may not reflect the real final wine composition, since no methodology ensures an extract like a wine.

The Spearman correlation coefficients were calculated between the WLJ phenolic compounds and both the grape characteristics (i.e., pH, total soluble solids, total acidity, and grape weight) and the total grape element profile (as calculated by Eq. 2) (Fig. S4). The elements B, Cu, K, Mg, Na, P, S, Si, Zn, Li were generally positively correlated ($p < 0.01$) with pH, CI and anthocyanins, many of them (i.e., Cu, Mg, Na, P, S, Zn, Li, Si) also with the tannins, and part of them (i.e., B, Cu, Na, S, Zn, Li) with the total phenols-IRPs. On the contrary, B, Cu, K, Mg, Na, P, S, Zn, Li were negatively correlated ($p < 0.01$) with the grape weight and the total acidity. These results suggest an association between several elements in grapes, their enological characteristics, and phenolic content.

The element profile of the WLJ is reported in Table 4, and the validation parameters in Tables S7 (Appendix D. Supplementary material). The element content of the WLJs was in the order: K > P > Ca > Mg > Si > Na > B > Fe > Cu > Zn > Mn ≥ Sr > Li. This order is the same as that found for the pulp and skin element profiles, except for Si, which was more concentrated than Na in the WLJ. A comparison with the literature (Catarino et al., 2018; Richardson & Chase, 2021) shows that the element profile of the WLJ is largely similar to that of certain red wines produced in neighbouring countries (Portugal, Spain, Croatia). To make inferences about the relationship between grapes and wine, the TCs were calculated by applying the Eq. 5. The TCs of elements were in the order: Li ≥ Mg > B > Fe > Si > Mn > P > Ca > Zn > Cu > K > Na > Sr (Table S8 and Fig. S5). Among the vineyards, very high variability (CV up to 76 %) was calculated for elements such as Li and Sr, while high variability for Fe, Mg, Mn, Si, Zn (CV below or around 50 %), moderate for P and Cu (CV below 30 %) and low for B, Ca and K (below or around 20 %). The possible preferential transfer of elements from a grape tissue rather than another was evaluated by calculating the Spearman correlation coefficients between the element content of the seeds, pulp, and skin *vs* the element content in the WLJ (Fig. S6). Highly significant correlations ($p < 0.001$) were found between the Mg and Sr content of the WLJ and that of the seeds, between the B, Ca, K, Mg, Mn, Na, Si and Sr content of the WLJ and that of the pulp, and between the K, Mg, Na, Si and Sr content of the WLJ and that of the skin. Therefore, it has been hypothesized a Mg and Sr transfer from all the grape tissues, a preferential transfer from the pulp and skin for K, Na, and Si, while only from the pulp the transfer for B, Ca, and Mn. Low correlation ($p < 0.05$) was found for Fe from the seeds and pulp, while no correlation was found for P and Cu between the grape tissues and WLJ.

3.4. Bioconcentration factors (BFs) in the grape seeds, pulp, and skin from the soil and their relationship with the grape characteristics and the WLJ phenolic compounds

The elemental uptake in the soil-plant system was evaluated using the BFs from soil to berry tissues (i.e., seeds, pulp, and skin) (Table S9), as calculated by Eq. 6 (reported in Section 2.4). Log-transformed BF values lower than 0 (Fig. 3) identify elements that are more abundant in the soil than in the grapes (Richardson & Chase, 2021), which suggests that the transfer of these elements to the berries is limited or reduced. In contrast, log BF values greater than 0 denote moderate to high element transfer to berries.

Compared with data reported by the literature (Angelova et al., 1999; Catarino et al., 2018; Milićević et al., 2018; Protano & Rossi, 2014; Richardson & Chase, 2021), the log BFs calculated for these Aglianico grapes are generally higher and identify elements bioconcentration, not previously reported, principally for B, Cu, Fe, K, P, S, Zn in all the tissues and secondarily for Mg only in the seeds. The discrepancy is due to the use in the previous works of pseudo-total (nitric and hydrochloric acid) and total (by hydrofluoric acid) digestion of soil samples, which dissolve more soil components (organic and mineral), resulting in an increased soil element concentration (Richardson & Chase, 2021), compared with the single extraction method with soluble salts used in this study. It is worth noting that the single extraction procedures give information on the "labile" elements in soil, and for that, they are more suitable for evaluations on soil-plant uptake of major and trace elements from agricultural soils and for predicting their influence on plants (Milićević et al., 2018).

The calculated BFs for the Aglianico grapes are consistent with the known needs of micro and macronutrients of all higher plants (Hänsch & Mendel, 2009). Below, a brief description of the elements' function for plant life, and the relationship, as calculated by Spearman's correlation coefficients, between the BFs, the grape enological characteristics, and the WLJ phenolic composition.

Potassium is the dominant cation in grape juice and accumulates at the highest rates after veraison (Rogiers et al., 2006). Accumulation of potassium has been supposed to assist in the drive for the accumulation of sugars into the berry and to contribute to the water uptake, especially after veraison (Hänsch & Mendel, 2009). Based on the log BF plots (Fig. 3) and data reported in Table S9, the K was always moderately enriched (from 0.6 to 1.2). Highly significant correlations ($p < 0.001$) were identified between the K BFs of the grape seeds, pulp, and skin and both the pH and the bound anthocyanins (Fig. S7). These correlations suggest that the higher the K uptake from the soil towards all the grape tissues, the more acidic the berries and the lower the content of

Table 4
Element profile of the wine-like juice (WLJ) and transfer coefficients from grapes to WLJ calculated for the TA DOCG terroir. The element content was reported as mg of element per liter of WLJ (mg L^{-1}) and in mg of element in the WLJ for kg of grapes used to produce the juice (mg kg^{-1}). These last data were used to calculate the transfer coefficients. Lowercase letters (a,b,c) were used to compare the mean ranks of the distributions in the TA terroir, according to Dunn's test ($p < 0.05$). The number of cases analysed for each vineyard is 12 (N = 12). ns = no significant differences according to Kruskal-Wallis analysis of variance by ranks.

Site	TA-A							TA-B							TA-S						
	Element profile					Transfer coefficients		Element profile					Transfer coefficients		Element profile					Transfer coefficients	
Element	Mean	±SD	Mean	±SD		Mean	±SD	Mean	±SD	Mean	±SD		Mean	±SD	Mean	±SD	Mean	±SD		Mean	±SD
	mg L^{-1}		mg kg^{-1}					mg L^{-1}		mg kg^{-1}					mg L^{-1}		mg kg^{-1}				
B WLJ	2.18	0.14	3.27	0.21	b	0.455	0.078	1.56	0.57	2.33	0.85	b	0.393	0.078	3.19	0.43	4.79	0.64	a	0.465	0.072
Ca WLJ	49.85	2.78	74.77	4.17	a	0.291	0.022	41.91	4.17	62.87	6.25	b	0.284	0.042	42.82	5.49	64.23	8.23	ab	0.269	0.056
Cu WLJ	0.51	0.19	0.77	0.29	ab	0.257	0.030	0.30	0.07	0.45	0.11	b	0.223	0.066	0.58	0.13	0.87	0.19	a	0.272	0.048
Fe WLJ	1.30	0.35	1.96	0.53	a	0.491	0.052	0.83	0.18	1.25	0.28	b	0.380	0.042	1.17	0.14	1.76	0.20	a	0.442	0.069
K WLJ	365.9	37.00	548.8	55.50	b	0.163	0.023	329.3	70.93	493.9	106.4	b	0.186	0.034	367.0	48.71	550.4	73.07	b	0.171	0.022
Mg WLJ	40.23	1.63	60.35	2.44	a	0.532	0.046	35.33	1.53	52.99	2.29	b	0.498	0.026	41.66	4.51	62.48	6.76	a	0.527	0.073
Mn WLJ	0.16	0.02	0.24	0.02	a	0.430	0.052	0.10	0.01	0.14	0.01	b	0.394	0.051	0.12	0.02	0.18	0.03	b	0.413	0.103
Na WLJ	3.44	0.85	5.16	1.27	ab	0.100	0.024	1.97	0.44	2.96	0.67	bc	0.062	0.014	1.77	0.26	2.65	0.40	c	0.055	0.008
P WLJ	60.92	9.71	91.38	14.56	ab	0.349	0.043	31.44	3.62	47.15	5.44	c	0.246	0.043	48.74	12.89	73.11	19.33	b	0.310	0.062
Si WLJ	6.46	0.61	9.70	0.91	a	0.476	0.077	5.17	0.49	7.76	0.74	b	0.532	0.062	3.40	0.74	5.11	1.11	c	0.416	0.110
Sr WLJ	0.14	0.02	0.21	0.04	ns	0.133	0.020	0.10	0.07	0.14	0.10	ns	0.094	0.042	0.12	0.01	0.18	0.02	ns	0.106	0.025
Zn WLJ	0.32	0.07	0.48	0.11	a	0.381	0.054	0.25	0.03	0.38	0.05	a	0.246	0.064	0.29	0.03	0.43	0.04	a	0.215	0.062
	µg L^{-1}		µg kg^{-1}					µg L^{-1}		µg kg^{-1}					µg L^{-1}		µg kg^{-1}				
Li WLJ	2.43	0.84	3.65	1.26	ns	0.532	0.309	2.67	2.69	4.01	4.03	ns	0.463	0.277	4.15	1.06	6.22	1.59	ns	0.564	0.235

Site	TA-O							TA-Y						
	Element profile					Transfer coefficients		Element profile					Transfer coefficients	
Element	Mean	±SD	Mean	±SD		Mean	±SD	Mean	±SD	Mean	±SD		Mean	±SD
	mg L^{-1}		mg kg^{-1}					mg L^{-1}		mg kg^{-1}				
B WLJ	2.82	0.59	4.23	0.88	ab	0.483	0.094	4.06	1.21	6.10	1.82	a	0.637	0.117
Ca WLJ	26.30	3.23	39.45	4.84	c	0.184	0.033	38.01	4.37	57.02	6.55	b	0.269	0.027
Cu WLJ	0.30	0.01	0.45	0.02	b	0.104	0.015	0.47	0.11	0.71	0.16	a	0.154	0.031
Fe WLJ	1.11	0.56	1.66	0.85	ab	0.656	0.318	0.98	0.12	1.47	0.18	ab	0.374	0.079
K WLJ	369.1	46.95	553.7	70.43	b	0.192	0.018	672.0	97.30	1008	146.0	a	0.280	0.048
Mg WLJ	49.56	26.16	74.33	39.23	a	0.556	0.247	50.18	11.90	75.27	17.85	a	0.599	0.124
Mn WLJ	0.09	0.04	0.13	0.06	b	0.548	0.290	0.14	0.03	0.21	0.04	ab	0.400	0.099
Na WLJ	5.45	1.65	8.18	2.48	a	0.383	0.135	5.30	1.37	7.95	2.06	a	0.210	0.057
P WLJ	15.81	3.66	23.71	5.49	c	0.061	0.018	78.28	16.97	117.4	25.45	a	0.449	0.102
Si WLJ	5.03	2.22	7.54	3.34	b	0.351	0.152	6.86	0.95	10.28	1.43	a	0.426	0.082
Sr WLJ	0.09	0.02	0.14	0.03	ns	0.114	0.015	0.21	0.17	0.31	0.26	ns	0.167	0.128
Zn WLJ	0.17	0.03	0.25	0.05	b	0.144	0.021	0.26	0.05	0.39	0.08	a	0.209	0.096
	µg L^{-1}		µg kg^{-1}					µg L^{-1}		µg kg^{-1}				
Li WLJ						–	–	7.34	5.01	11.01	7.52	ns	0.661	0.439

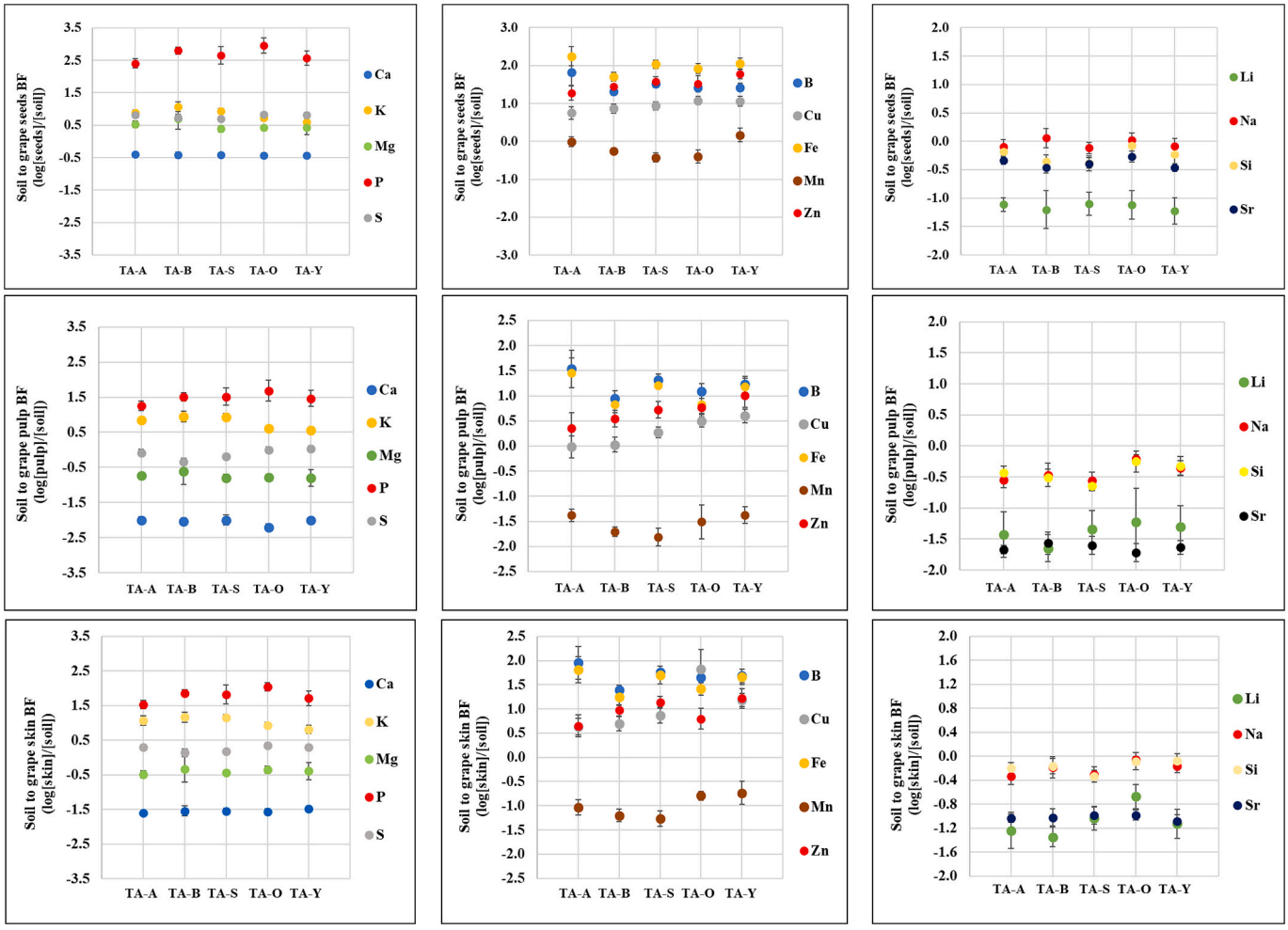

Fig. 3. Bioconcentration factor (BF) of nutrients (Ca, K, Mg, P, S, B, Cu, Fe, Mn, Zn), beneficial (Na, Si) and other elements (Li, Sr) from soils (bioavailable content) to grape seeds (a,b,c), pulp (d,e,f) and skin (g,h,i) of the Taurasi terroir, plotted on logarithmic scale. Each point is the mean ($n = 12$), and bars are the ranges of the standard deviation.

polymeric pigments (i.e., bound anthocyanins), which are generally considered a wine quality trait. These correlations are also consistent with the findings of previous studies reporting that acidic grapes are generally not preferred for the Taurasi wines (Picariello et al., 2019).

Magnesium (Mg) is an important macronutrient, with several physiological functions in the plant being strongly connected with photosynthesis (Mengel & Kirkby, 2004). The log Mg BFs were limited in the skin (from −0.5 to −0.3) and moderate in the seeds (from 0.4 to 0.7) (Fig. 3). Highly significant correlations ($p < 0.001$) were found between Mg BFs and both the CI and berry weight (Fig. S7).

Phosphorus is an essential macronutrient for plant growth and development (Mengel & Kirkby, 2004). Nevertheless, appropriate reduction in phosphorus fertilization has been found to enrich the anthocyanin concentration of grape berries and, consequently, to improve the quality of the resulting wine (Jezek et al., 2018). The log P BFs were moderate in the pulp (1.3–1.7) and the skin (1.5–2.0), but high in the seeds (2.4–3.0). However, only the P BF of the pulp was found to be positively correlated ($p < 0.05$) with anthocyanins, tannins, and IRPs content of the WLJ, while negatively correlated ($p < 0.05$) with the hue and berry weight (Fig. S7).

Regarding the presence of sulphur and copper in grapes, it is likely due to their use in viticulture as antibacterial (Pateraki et al., 2007) and fungicidal agents, respectively. Powdery mildew, caused by Erysiphe necator, is one of the most damaging diseases of the grapevine (*Vitis vinifera* L.), resulting in reduced yield and increased susceptibility to bunch rots, as well as imparting unfavourable sensory characteristics to wine. Although organic viticulture relies on the use of S to control grapevine powdery mildew, concerns have been raised about its negative impact on beneficial arthropods and microorganisms (Prischmann et al., 2005). Copper fungicides are widely used in viticulture, as grapevines are plagued by downy mildew, Plasmopara viticola, every year. Copper is also of utmost importance to plant life, as it is essential for photosynthesis, mitochondrial respiration, carbon and nitrogen metabolism, etc. (Hänsch & Mendel, 2009). Nevertheless, Cu accumulates in the soil over time as a result of plant treatments. Under rainy or windy conditions, particles are removed from the ground and deposited onto the vine canopy. This contaminates the open stomata, resulting in a decline in grape leaf gas exchange and an increase in plant stress. This effect has been found to reduce grape quality and grape sugar content (Jermini et al., 2010). Reduced log S BFs were observed for the pulp (from −0.3 to 0.03) and the skin (0.1–0.4), while moderate log S BF values were found in the seeds (0.7–0.8). The S BFs of seeds, pulp, and skin were significantly and positively correlated ($p < 0.01$) with the grape pH and the bound anthocyanins, while only the S BFs of the pulp were correlated with the tannins. On the contrary, negative significant correlations ($p < 0.001$) were identified between the S BFs of all grape tissues and the total acidity, and only the S BFs of pulp and skin were correlated with the berry weight. Copper was moderately bioconcentrated in the seeds (log BFs ranging from 0.8 and 1.1) and the skin (0.6 to 1.8), while the Cu BFs were limited in the pulp (from −0.01 to

0.5). The Cu BFs of all tissues were positively correlated ($p < 0.01$) with pH, anthocyanins, tannins, and total phenols-IRPs, while being negatively correlated with total acidity. Hence, these results suggest that the higher the BFs of both S and Cu, the higher the grape quality traits. It is likely that antibacterial and fungicidal compounds based on S and Cu have a positive effect on preserving grapes and maintaining their quality. It does not seem that the adverse effects of soil contamination by Cu mentioned above have occurred on grape quality in the TA vineyards.

Iron is of great importance to plant life. It is a redox-active metal involved in photosynthesis, mitochondrial respiration, nitrogen assimilation, etc. (Hänsch & Mendel, 2009). Boron is an essential component of many processes, including protein synthesis, sugar transport, respiration, RNA metabolism, carbohydrates, plant hormones, and cell wall synthesis (Hänsch & Mendel, 2009). Iron and B were found highly enriched in the seeds (log Fe BFs ranged from 1.7 and 2.2 and log Cu BFs from 1.3 and 1.8), the pulp (0.8–1.4 and 0.9–1.5, for Fe and Cu, respectively), and the skin (1.4–1.8 and 1.4–2.0). Iron BFs in the seeds and the skin were found positively correlated with the WLJ anthocyanins content ($p < 0.05$ and $p < 0.01$, respectively), as well as the B BFs in the pulp and skin ($p < 0.01$).

Manganese and Zn are important elements for plant metabolism, as they occur in several enzymes for protein synthesis and energy production (Hänsch & Mendel, 2009). Manganese can act as a catalytically active metal or exert an activating role on enzymes (Barber, 2003), while Zn plays an important role in seed development, and a deficiency can delay plant maturity. The Mn was never enriched in the grape tissues (log Mn BFs ranged from 0.4 to −2.4). A positive significant correlation was found between Mn BFs of the pulp and the skin ($p < 0.001$) with the pH and bound anthocyanins, and a negative correlation with the total acidity ($p < 0.001$). On the contrary, the Zn was moderately enriched in the pulp (log Zn BFs in the range 0.4–1.55) and the skin (0.7–1.2), but highly in the seeds (1.5–1.8). For the Zn BFs of all tissues, positive significant correlations ($p < 0.001$) were found with the CI, anthocyanins, and total phenols-IRPs, while for the BFs of the seeds and pulp, correlations ($p < 0.001$) were also found with the pH and tannins (Fig. S7). These data for Mn and Zn suggest that higher uptake of these elements results in higher-quality traits of grapes and WLJ.

Sodium, as well as Si, Co, Se, and Al, are considered beneficial elements since they promote plant growth, improve crop productivity, and enhance plant nutritional value (Pilon-Smits et al., 2009). Due to the similarity of Na^+ to K^+, Na^+ can replace K^+ as osmoregulator for stomatal movement and cell expansion when K levels are limiting. Other than halophytic and natrophilic species, low levels of Na can have beneficial effects on plant growth under moderate abiotic stress (i.e., drought stress). The log Na BFs were found to be close to 0 only for the seeds and were always below 0 for the pulp and skin, meaning that Na is not accumulated in the berry tissues. A positive significant correlation ($p < 0.01$) was found between the Na BFs of the skin and pulp with the tannins and total phenols-IRPs.

Silicon is one of the most abundant elements of the crust surface and is available for plants as monosilicic acid, $Si(OH)_4$. It is deposited throughout the plant as amorphous silica in the cell walls, enhancing their rigidity and strength. The effect of the Si on plant health concerns its role in reducing plant susceptibility to fungal disease and in preventing abiotic stress (Liang et al., 2007). The Si bioconcentration was limited in the seeds (log Si BFs ranging from −0.4 to −0.1) and skin (from −0.3 to −0.1). Positive significant correlations ($p < 0.001$) were found between Si BF of seeds and pulp with pH and bound anthocyanins, while negative with the total acidity; moreover, the Si BFs of the pulp and skin were correlated ($p < 0.01$) with the tannins (Fig. S7). Considering that the higher the Si BF, the higher the grape acidity and anthocyanins, the data suggest a positive role played by the Si on grape and WLJ quality traits.

Although Li is not known to be an essential plant nutrient, there is some evidence that Li can affect plant growth and development (Angino et al., 1974). Increased Li concentration in soil is toxic to some plant species. Citrus trees are known to be the most susceptible to injury by an excess of Li (Gough et al., 1979). In the case of the Taurasi grapes, no uptake was found in the grape tissues (log Li BFs less than −0.8). Several positive correlations ($p < 0.001$) were identified between the Li BFs of the pulp and skin with the CI, pH, the bound and total anthocyanins, and negative correlations between the Li BFs of skin and pulp with the berry weight ($p < 0.001$) and total acidity ($p < 0.05$).

About Sr, there are not many reports of its toxicity in plants, despite it being a relatively common trace element in the Earth's crust. Plants vary in their tolerance to this element. Toxic Sr level for plants has been fixed at 30 ppm (AW)(Shacklette et al., 1978). However, there is no evidence that stable Sr, at levels present in the biosphere, has any deleterious effect on man and animals. Limited log Sr BFs were found for all grape tissues (Fig. 3), and no significant correlation was found between Sr BFs and grape and WLJ characteristics.

3.5. Relationship between grape enological characteristics/composition and soil chemical/physical properties

A principal component analysis (PCA) was carried out to explore the relationships between several variables, including the soil chemical and physical properties, enological characteristics, main phenolic compounds of the WLJ, and the BFs of the elements from the soil to the grape tissues. This analysis aimed to infer the potential impact of the soil characteristics on the quality traits of grape and wine production. Since we do not know a priori whether the grape characteristics are more influenced by the surface-exploring roots or the deeper ones, we examined the relationships separately for soil depths of 0–30 and 30–70 cm (Fig. 4a and 4b, respectively). The first two components (sum of PC1 and PC2) accounted for 45 and 46 % of the total variability, in the soil depths 0–30 and 30–70 cm, respectively. The low values of explained variability suggest quite high homogeneity of grape and soil characteristics among the vineyards, confirming the uniqueness and peculiarity of the Taurasi terroir. Nevertheless, along the PC1 (accounting for 28 and 27 % of the total variability, for 0–30 and 30–70 cm of depth, respectively), TA-O and TA-Y vineyards (both from the Mirabella Eclano village) separated on the positive scores from all the others, i.e., TA-A, TA-B, TA-S (from Montemarano village), on the negative scores (Fig. 4). Assuming a loading cut-off value of $|0.40|$ for selecting the most influential variables for each component (Table S10), PC1 and PC2 are featured as follows.

The positive scores of the PC1 (Fig. 4c, d, e, f, g) were characterised by the association made by (loadings in brackets): CI (0.40), grape pH (0.78), anthocyanins (0.89 and 0.54 for bound and total, respectively), tannins (0.70) and total phenols-IRPs (0.44), soil pH (0.55), EC (0.79), total carbonates (0.54), silt content (0.89), K_{ex} and Na_{ex} (0.79 and 0.61, respectively), ESP (0.68), the BFs of some nutrients, including Cu (0.66, 0.81 and 0.53), P (0.53, 0.59, 0.55) and S (0.58, 0.81, 0.72) in the seeds, pulp and skin, respectively, and Zn in the pulp (0.46); beneficial elements like Si (0.74, 0.79 and 0.53) in the seeds, pulp and skin, and Na (0.55 and 0.38) in the pulp and skin, and other elements like Li in the pulp and skin (0.71 and 079) and Sr in the seeds (0.48). On the contrary, on the negative scores association was found for total acidity (0.80) and berry weight (0.72), with the sand (0.85), Ca_{ex} (0.67), CEC (0.46) and the BFs of K (0.62, 0.67, 0.54 in seeds, pulp and skin, respectively). The results showed that clayey soils with higher silt content, but also higher carbonate content, pH, ESP, and Na_{ex}, are associated with the production of grapes characterised by higher quality traits concerning pH, content of main phenolic compounds, and CI. It is worth noting to find that these grape quality traits are associated with higher bioconcentration rates of some nutrients (P, S, Zn, Cu), beneficial (Si and Na), and other elements (Sr and Li) in grapes. On the contrary, clayey soils with higher sand content, but also higher CEC and exchangeable Ca, produce heavier grapes with higher total acidity, and mainly K bioconcentration in all the tissues. It is well known that soil texture plays a key role in forming the pore network and the soil structure. These, in

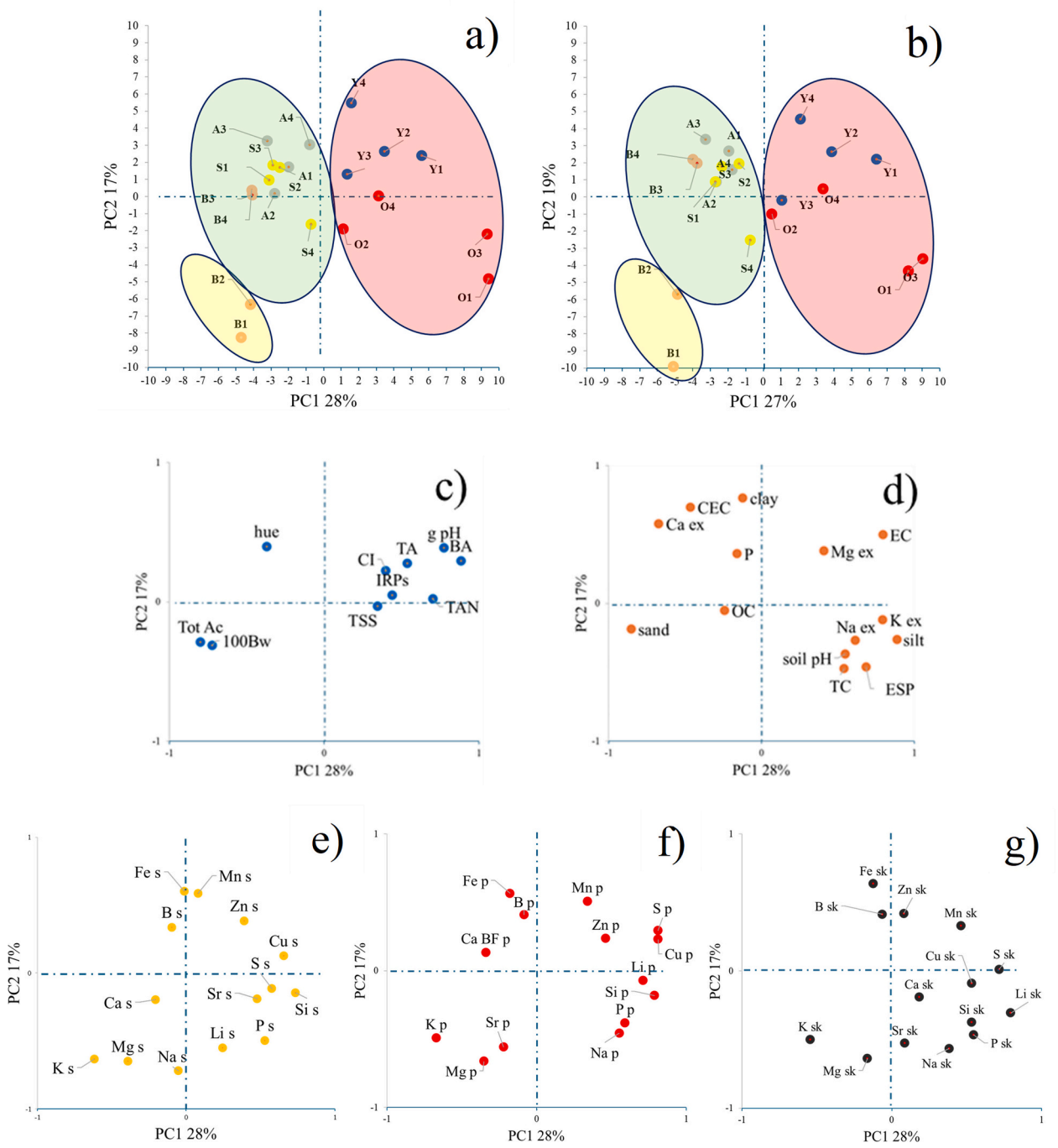

Fig. 4. Principal component analysis (PCA) obtained by data of the main soil chemical and physical properties, the grape enological characteristics, the wine-like-juice (WLJ) phenolic compounds, and the bioconcentration factors (BFs), in the 4 points ($n = 3$ at each point) of each vineyard. Vineyard label names were shortened (i.e., TA-A = A; TA-B = B; TA-S = S; TA-O = O; TA-Y = Y) to avoid superposition masking labels. In a) and b) are reported the projections of the five vineyards at both 0–30 and 30–70 cm of soil depth, respectively. From c) to g) the projection of variables for the depth 0–30 cm. Specifically, in c) the enological grape characteristics and WLJ phenolic compounds; in d) the soil chemical and physical properties in e), f) and g) the bioconcentration factors of elements from soil in seeds (s), pulp (p) and skin (sk), respectively.
Legend: soil pH: pH (H_2O); EC = electrical conductivity; OC = organic carbon; P = available phosphorous; CEC = cation exchange capacity; Ca_{ex}, K_{ex}, Mg_{ex}, Na_{ex} = exchangeable Ca, K, Mg and Na; ESP = exchangeable sodium percentage; silt, clay, sand = soil texture; TC = total carbonates; CI = color intensity, TSS = total soluble solids, 100 Bw: weight of 100 berries, g pH = grape pH, Tot Ac = total acidity; BA = bound anthocyanins, TA = total anthocyanins, TAN = tannins, IRPs = total phenols.

turn, regulate water holding capacity, aeration, gaseous diffusion, and water movement (Kiuru et al., 2022). The CEC is a parameter related to soil fertility, as it refers to the soil's ability to hold (and exchange) cations by electrostatic attraction (Wijayawardena et al., 2016). Likely, the greater sand content in these clayey soils and the higher soil fertility produce conditions of higher soil available water and improved nutrient status to plants that directly affect grape weight and acidity. A positive correlation between the soil sand content and the total acidity of grapes has also recently been highlighted for the Nero d'Avola grapes (Bambina et al., 2024). Furthermore, the direct relationship between the soil EC

and both the grape pH and all the phenolic compounds, and inverse with the berry weight and the total acidity, seems to suggest that not only the available soil water content, identified in the correlation with the soil texture, but also the quality of the soil water can affect the grape quality. Indeed, the soil EC is closely related to the soil salinity, and high EC values can indicate excess salts in the soil, hindering plant growth and reducing crop yields. On the contrary, our results showed that berry and WLJ quality traits, including anthocyanin content and grape pH, were positively correlated with higher EC values, in contrast with the results of Bambina et al. (2014) identfying a negative correlation between EC and anthocyanin content.

Along the PC2 (accounting for 17 and 19 % of the total variability, in the 0–30 and 30–70 cm of soil depth, respectively), separation was found between TA-O and TA-Y, located in the same village. The two vineyards have opposite exposure (TA-O is on the NW and TA-Y on the SE), which is likely to affect the characteristics of the grape. The positive scores of the PC2 were characterised by the association of clay content (0.77), CEC (0.70), Ca_{ex} (0.58), EC (0.50), grape pH (0.40), the BFs of several nutrients like Fe for the seeds, pulp and skin (0.60, 0.57 and 0.64, respectively), B in the pulp and skin (0.41 and 0.41, respectively), Mn in the seeds and pulp (0.59 and 0.51, respectively), Zn in the skin (0.42). This association of higher bioconcentration of nutrients (Fe, B, Mn, Zn) in grapevines grown on finer (more clayey) soils is consistent with the results on the positive scores of the PC1, including grape quality traits. Worth noting, on the positive scores of the PC2 we find the TA-Y vineyard, the one with the SE exposure, the one providing the grapes with the best quality traits. However, since the PC2 explained only 17–19 % of the total variability, the identified differences between the two vineyards must be considered with caution, and quite homogeneous their soil properties and the grape characteristics.

4. Conclusions

A comprehensive study on the soil-grape-wine system was conducted across five vineyards of the Taurasi wine terroir in southern Italy. The novelty of this work lies in the multiparametric analysis aimed at studying the complexity of the terroir effect on the chemistry and quality traits of grapes and wine. The ANOVA has shown a general homogeneity of soil and grape composition across the vineyards, confirming the unique identity of the Taurasi terroir. Notably, Fe was found among the elements that accumulated mostly in the seeds, alongside Mn, Cu, and Zn. As these elements can influence various processes in wine, the awareness of their distribution across grape tissues offers valuable guidance for optimizing winemaking practices and avoiding possible undesirable wine faults. Overall, the B, Cu, Mg, P, S, Si, Zn concentration in grapes was significantly correlated with several grape quality traits, including the berry weight, grape pH, and the main phenolic compounds. Concerning the nutrients B, Mg, P, and Zn, this finding supports the perception that good plant nutrition positively impacts the grape quality. Regarding S and Cu, the results align with their known protective effects through vineyard treatments, preserving grape quality traits.

The WLJ (wine-like-juice) extracts used as a wine proxy of the Taurasi terroir showed elemental profiles comparable to those of European red wines, supporting their utility for preliminary assessments of potential wine composition. Estimation of the transfer coefficients from the grape tissues to the WLJ highlighted potential migration of K, Mg, Na, Si, and Sr from the pulp and the skin into wine, emphasizing the importance of early detection to prevent quality defects. However, the WLJ remains a simplification and cannot fully replicate wine complexity. Bioconcentration factors for Fe, B, Zn, and Cu were consistent across grape tissues and vineyards, indicating uniform uptake within the terroir. The PCA further linked uptake of nutrients (Mn, Cu, Zn, P, S), beneficial elements (Na, Si), and Li to enological parameters (pH, total soluble solids, color intensity, main phenolic compounds), and to specific soil properties (electrical conductivity, exchangeable Na and K, silt content, pH, total carbonates). These findings reinforce the pivotal role of terroir in shaping grape chemistry. Future studies should broaden the sampling of the Aglianico cultivar within the Taurasi area to support terroir-based classification using supervised pattern recognition models.

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CRediT authorship contribution statement

Simona Vingiani: Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Investigation, Conceptualization. **Fiore Capozzi:** Writing – review & editing, Visualization, Validation, Software, Data curation. **Angelita Gambuti:** Writing – review & editing, Supervision, Methodology. **Pasquale Ruocco:** Investigation, Formal analysis. **Annina Caputo:** Methodology, Investigation, Formal analysis.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2025.145433.

Data availability

Data will be made available on request.

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