OENO One
vine & wine

DOI: https://doi.org/10.20870/oeno-one.2026.60.1.9411

OPEN ACCESS

ENOLOGY ORIGINAL RESEARCH ARTICLES

A first characterisation and classification of Montalcino wines in relation to production areas: combination of destructive, non-destructive and chemometrics analyses

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Article number: 9411

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Associate editor:
Tristan Richard

Received:
7 May 2025

Accepted:
12 November 2025

Published:
5 January 2026

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ABSTRACT

Sangiovese (*Vitis vinifera L.*) is one of Italy's most important wine grape varieties, forming the basis of several iconic DOCG wines, including Chianti, Chianti Classico and Brunello di Montalcino. The production of Brunello di Montalcino is confined to a well-defined area in Tuscany, which can be further divided into four macro-zones that may influence the wine's distinctive characteristics. However, potential compositional differences among the wines from these subzones have not yet been thoroughly explored. This study aimed to characterise Brunello di Montalcino wines from the four sub-areas in terms of their phenolic and aromatic profiles. Analyses were conducted using conventional techniques such as HPLC-DAD and GC-MS, alongside the non-destructive approaches electronic nose (E-nose) and AOTF-NIR spectroscopy. These latter tools were evaluated for their ability to differentiate wines based on their geographical origin. The results revealed pronounced differences among wines from the four subzones, particularly within specific phenolic classes and volatile compound profiles. Non-destructive methods showed promising discriminatory power in distinguishing wines according to their macro-area of origin. This study provides a deeper understanding of how intra-regional geographical differences within the Brunello di Montalcino DOCG influence wine composition and aromatic expression, and thereby reinforce the wine–terroir relationship. The results contribute to broader zoning objectives by enhancing communication of territorial identity, promoting quality through differentiation, informing consumers about grape origin, and fostering market interest through a more diversified product offering.

KEYWORDS: Sangiovese, production area, polyphenols, aromatic profile, E-nose, NIR

INTRODUCTION

Sangiovese (*Vitis Vinifera* L.) is the main cultivar in the winemaking region of Tuscany. It is the main winegrape variety in 33 different denominations of origin (DOC and DOCG) and its cultivation occupies more than 60 % of the total vineyard area (Fregoni *et al.,* 2006). The province of Siena (Central Tuscany) comprises about 14,500 ha of vineyards and produces some of the world's most renowned DOC Sangiovese-based red wines, such as Brunello di Montalcino, Chianti, Chianti Classico, and Nobile di Montepulciano. The production disciplinary of these appellations imposes Sangiovese as the main or only grape variety to be used in wine production (Buccelli *et al.,* 2010). In the province of Siena, the relationship between wine and territory is extremely important. A notable example is the town of Montalcino, which, due to the commercial success of its wine, has quickly become a model for business and an important tourist destination (Consorzio di tutela Brunello di Montalcino, 2023). In 1966, Brunello di Montalcino was one of the first wines to receive the DOC designation in Italy. The following year, a consortium of local producers was formed with the goal of maintaining high quality standards of Brunello di Montalcino wines. In 1980, Brunello was promoted to DOCG status, thus becoming the first Italian wine to receive this prestigious designation. The success of Brunello is clearly reflected in its increased production over the years; for instance, in 1975, 25 producers in Montalcino produced around 800,000 bottles of wine, and by 1995 the number of producers had risen to 120 and production to 3.5 million bottles. Currently, annual sales exceed 4 million bottles, generating approximately 150 million euros, with one-third from the Italian market and the rest from abroad (70 % in 2023), led by the USA (30 %), Switzerland and Germany (20 %), Canada (12 %), and South America (8 %) (Consorzio di tutela Brunello di Montalcino *et al.,* 2023). According to the production regulations, Brunello di Montalcino DOCG must be made exclusively from Sangiovese "grande" grapes cultivated in the designated area, with a maximum allowed yield of 8000 Kg of grapes per hectare a maximum wine yield of 68%. The vines are trained using either the spurred cordon or the "archetto" (modified Guyot) system. The wine must be bottled in Bordeaux bottles and required minimum alcohol content is 12.5% by volume. Brunello di Montalcino wine must be aged for at least 24 months in oak, with an additional 4 months in bottle (6 months for the reserve). It can be marketed only 5 years after its production (6 years for the reserve). The wines are generally characterised by a ruby red colour, which tends to garnet with aging, a characteristic aroma with an intense fragrance, and a dry, warm, slightly tannic, robust, and harmonious flavour. Thus, the Montalcino region is recognised as the perfect terroir for Sangiovese grapes to express their varietal characteristics. In a previous study (Buccelli *et al.,* 2010), 79 experimental vineyards in Chianti classico, Chianti colli Senesi, and Vino Nobile di Montepulciano were evaluated to identify the best soil characteristics for high quality Sangiovese based on vine performance; the Montalcino region was found to be the most suitable for the production of high-quality wines.

The Brunello di Montalcino DOCG wine region can be subdivided into four macro-areas as shown in Figure 1. This subdivision is particularly relevant in the current market context, where there is growing interest in enhancing the value of agri-food products by specifying their geographic origin, thereby reinforcing their exclusivity. This approach aligns with the concept of zoning, which involves dividing a production area into homogeneous subregions based on ecological and geographical characteristics. These factors can influence the behaviour of the crop and, consequently, the qualities of the resulting products. Zoning procedures generally require an integrated analysis of environmental conditions, genetic factors, agro-technological practices, and processing operations, as well as the qualitative assessment of the final product, resulting in a more precise and rational categorisation of the territory based on its suitability for specific crops. A striking example of this aspect is provided by the consortium of Chianti Classico, a neighbour of Brunello di Montalcino, which in 2023 subdivided the Chianti Classico production territory into smaller areas known as Additional Geographical Units (UGAs). Since then, the UGA name is cited on the Chianti Classico labels, thus giving even more importance to the link between the territory and the wines (Consorzio vino del Chianti classico, 2023). Therefore, zoning a wine production area strengthens communication about the wine-territory binomial, increasing quality in terms of identity and territoriality, and allowing the consumer to know the origin of the grapes and stimulating demand by differentiating the offer (Costantini *et al.,* 2008). Several approaches have been applied to differentiate wines according to *terroir*, combining chemical markers with multivariate statistics. In particular, phenolic compounds have often been investigated as key biomarkers due to their strong dependence on grape variety, environmental factors, and vineyard management, thus providing reliable indicators of geographical origin (Urvieta *et al.,* 2021). Likewise, aromatic profiles have been used to highlight terroir-related differences (Bedreag *et al.,* 2025), reflecting both grape metabolism and winemaking practices. In parallel, non-destructive analytical techniques such as near infrared spectroscopy (NIR) (Geană *et al.,* 2019) and electronic nose (E-nose) (Marques *et al.,* 2024) have demonstrated high potential for rapid and robust terroir discrimination when coupled with chemometric models.

In this context, this study aimed to undertake an initial characterisation of Brunello di Montalcino DOCG wines from the four distinct areas delimited by the production regulations. The objective was to obtain preliminary information about the influence of the territory on the phenolic and aromatic profiles of wines and whether it can serve as a basis for formal zonation. The study involves traditional analysis HPLC-DAD and GC-MS, and the non-destructive techniques E-nose and NIR spectroscopy. This approach aims to uncover the subtle yet distinctive chemical profiles associated with the different production areas, thereby contributing to a deeper understanding of the complexities and territorial expression of Brunello di Montalcino wines, despite the overall similarity of their compositional characteristics.

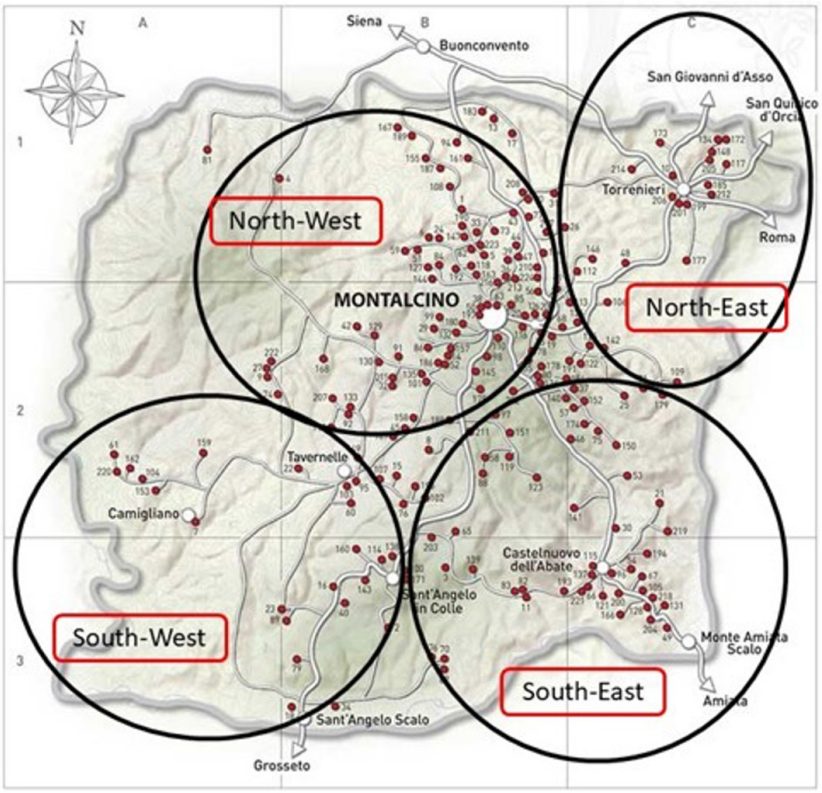


FIGURE 1. Subdivision of the four areas of Montalcino: North-West, North-East, South-West and South-East quadrants.

MATERIALS AND METHODS

1. Sampling and experimental design

Sampling was carried out in 20 different wineries, which all produce wines through spontaneous fermentation. The selection included five wineries from each of the four macro-areas of the Montalcino region: South-West (SW), South-East (SE), North-West (NW), and North-East (NE). Each sampled wine was produced using grapes grown exclusively in the corresponding macro-area in full compliance with the Brunello di Montalcino DOCG production regulations. In each zone, five wines (one from each winery) from the 2021 and 2022 vintages and destined to become Brunello di Montalcino DOCG were sampled (0.75 L) directly from their aging tanks. Samples were filtered at 0.45 µm and temporarily stored at 4 ± 0.5 °C until analysis. Each sample was analysed using paired methodologies: E-nose and VOCs were measured on the same aliquot, while NIR and polyphenols were assessed on another aliquot of the same sample. It was decided to sample the wines at this early aging stage, rather than after the minimum barrel aging period required by the DOCG regulation, in order to capture the intrinsic characteristics of the wines - as influenced by their respective growing areas - before being subject to any potential homogenising effects of extended aging.

2. Analytical determination

2.1. Polyphenol profile

The polyphenol profile was analysed using high-performance liquid chromatography (HPLC) using the Watherouse method (Ritchey *et al.,* 1999). The HPLC system had four solvent pumps (P680) and a PDA 100 as a detector. A C-18 column (Dionex Acclaim 120 C18, 5 µm, 4.6 × 250 mm) was used as the stationary phase at 40 °C. The mobile phases (flow rate of 0.5 mL min^{-1}) were: Solvent A, 50 mmol L^{-1} ammonium dihydrogen phosphate adjusted to pH 2.8 with orthophosphoric acid; Solvent B, 20 % solvent A with 80 % acetonitrile; Solvent C, 0.2 mol L^{-1} orthophosphoric acid adjusted with NaOH at pH 1.5. For qualitative and quantitative analysis of the individual polyphenols, calibration curves were prepared using 33 selected analytical standards (purity 99 %, Sigma-Aldrich Milan, Italy), which were chosen to represent the major phenolic classes in grape and wine matrices (namely anthocyanins, flavonols, flavanols, phenolic acids, and stilbenes). The measurements were performed in triplicate.

2.2. Total polyphenols, anthocyanins and flavonoids

Total polyphenol content (TPC) was measured using the colorimetric method Folin–Ciocalteu (Singleton *et al.,* 1965). Polyphenol content was determined by interpolating the registered data with those obtained from the calibration curve ranging between 312.5 mg/L and 5000 mg/L. The content was expressed as milligrams of gallic acid equivalents (GAE)/ L^{-1} of wine. Total anthocyanins were measured by dilution with hydrochloric ethanol and expressed as mg/L malvidin equivalent (Di Stefano *et al.,* 1989). Total flavonoid content (TFC) was measured using the colorimetric method of (Zhishen *et al.,* 1999) and expressed as mg of flavonoids/l^{-1} of wine, determined against a catechin calibration curve ranging between 75 mg/L to 1000 mg/L. Analyses were performed in triplicate.

2.3. Aromatic profile

The aromatic profiles of the wine samples were analysed using 5 mL of each sample. Headspace solid-phase analysis was performed using a PerkinElmer Clarus® SQ 8 GC/MS system, and ionisation source electron ionisation (EI) at 70 eV, coupled with a PerkinElmer Turbomatrix™ HS-40 autosampler. For headspace sampling, 20 mL glass vials (PerkinElmer Inc., Italy) sealed with aluminum crimped caps and PTFE-coated silicone gaskets (PerkinElmer Inc., Italy) were used. Samples were thermostated at 80 °C for 15 minutes prior to injection, with a headspace pressure of 30 psi, needle temperature set at 90 °C, and transfer line temperature at 110 °C. The vial pressurization time was 1 minute, followed by an injection time of 0.02 minutes. Chromatographic separation was carried out using an Elite capillary column (30 m × 0.25 mm × 0.25 µm). Injections were performed in splitless mode at 220 °C, with nitrogen as the carrier gas under constant pressure (25 psi). The oven temperature programme was as follows: initial temperature of 40 °C for 2 minutes; ramped at 5 °C/min to 110 °C and held for 3 minutes; then ramped at 10 °C/min to 230 °C and held for 2 minutes. Total run time was 33 minutes, with a withdraw time of 0.20 minutes. Mass spectrometric detection was conducted with a GC inlet line temperature of 200 °C and an ion source temperature of 180 °C. Data were acquired in full scan mode across an m/z range of 35–400, with a scan time of 0.20 seconds and an interscan delay of 0.05 seconds. Volatile compounds were identified by comparing the acquired mass spectra with those in the NIST 98 mass spectral database (Version 2.0, USA), selecting only compounds with a match quality of 80% or higher. Peak integration and quantification were performed using TurboMass software (TurboMass R, Version 5.4.2, PerkinElmer Inc., USA, 2008). The area of each peak was normalized to the total peak area. All measurements were performed in triplicate.

3. Electronic Nose

The electronic nose (E-nose) used was designed, developed and assembled at the University of Rome Tor Vergata and is based on an array of 12 quartz microbalances (QMBs). In these sensors, small changes in mass (Δm) on the absorbing layer of the quartz surface lead to a shift in frequency (Δf) in the electrical output signal of the oscillator circuit. Within a range of minor alterations, the change in frequency (Δf) is directly proportional to the change in mass (Δm). The chosen QMBs are made from AT-cut quartz crystals with a fundamental frequency of 20 MHz, corresponding to a mass resolution of a few nanograms (Santonico *et al.,* 2010). The QMBs were functionalised by seven metal complexes (Mg, Co, Cu, Zn, Fe, Mn, and Sn), free base (H2) of 5, 10, 15, 20-tetrakis-(4-butyloxyphenyl) porphyrin (TBPP), free base (H3), copper, phosphorus and manganese complexes of 5,10,15-triphenylcorrole (TPC) (Capuano *et al.,* 2023). The sensing molecules were synthesised and characterised in the Department of Chemical Science and Technology at the University of Rome Tor Vergata (Capuano *et al.,* 2020; Nardis *et al.,* 2019; Capuano *et al.,* 2015). Each QMB is individually linked to an oscillator circuit. A temperature-compensated quartz crystal is used as a reference for measuring oscillator output frequencies, providing a frequency resolution of 0.1 Hz. Gas delivery is managed through a tubeless embedded pneumatic system that incorporates a poly(methyl methacrylate) manifold with two inlets and one outlet. This system is connected to a miniature diaphragm pump (flow range 0–200 sccm), a three-way electronic valve, a proportional electronic valve and a flow sensor. The acquisition of data, instrument functions and settings are all controlled using proprietary software developed in Matlab (Muñoz-Castells *et al.,* 2023). Wine measurement was carried out as follows: 5 mL of wine was incubated in 20 mL closed glass vials (equipped with silicon septum) at 30 °C for 20 min. Then, the equilibrated headspace was extracted for 90 seconds using a stream of filtered air and delivered into the electronic nose. After each measurement, a pure air stream was used to clean the E-nose for an additional 300 seconds, establishing the reference signal. Sensor signals were calculated as the resonant frequency shift between the two steady conditions corresponding to sensors exposed to pure air and the sample. The ensemble of sensor signals is composed of patterns (fingerprints) encoding the global composition of the headspace. The measurements were performed in triplicate.

4. NIR spectral acquisition

The same wines used for E-nose evaluation were employed in NIR spectral analysis, which was performed by using an NIR–acousto-optic tunable filter (AOTF) spectrophotometer (Luminar 5030 miniature hand-held NIR analyser, Brimrose, Baltimore, MD, USA).

The readings were taken from each wine sample, using the transmittance method in the range of 1100–2300 nm, with wavelength increments of 2 nm. Ten spectra were acquired in transmittance (T) for each wine sample and then averaged to obtain a representative spectrum.

5. Data analysis

Analytical data were analysed through the Shapiro–Wilk and Bartlett test to verify normality and homogeneity of variances. Once these prerequisites were established, data were compared by one-way ANOVA and Tukey's HSD post hoc test with $p \leq 0.05$, using R version 4.0.1. Polyphenols and volatile compounds data were autoscaled and used to build principal component analysis (PCA) with Venetian blind (blind thickness = 1) as the validation method. E-nose numerical data were pre-treated with two normalisation filters (mean centering and autoscaling) and then used for a partial least square discriminant analysis (PLSDA) with Venetian-blind as validation method (blind thickness = 1). Finally, raw spectra of NIR measurement were transformed to absorbance (Abs = log 1/T) and then averaged to obtain a representative spectra for each sample using SNAP! 2.03 software (Brimrose). The spectra were then used for a PLSDA using venetian-blind as a validation method (blind thickness = 1). Multivariate analyses were carried out using Matlab R2013a (MathWorks®, Natick, MA, USA) and PLS Toolbox (Eigenvector Research, Inc., Manson, WA, USA).

RESULTS AND DISCUSSION

1. Phenolic profile

The twenty wines were analysed for their phenolic composition; the average, minimum and maximum values for each zone are reported in Table 1. The four production areas showed similar global phenolic composition. However, small differences were observed in the minimum values of total polyphenols, flavonoids and anthocyanin. For instance, the SW area had the lowest value of total polyphenols, approximately 30 % lower than the SE area. On the other hand, in the SE zone the minimum content of flavonoids was observed, which was about 18% lower than SW zone.

Through HPLC analysis, 26 phenolics comprising non-acylated anthocyanins (Table S1), quercetins (Table S2), flavanols (Table S3), phenolic acids (Table S4), and non-flavonoids stilbenes (Table S5) were identified in the different wines. The phenolic profile of wines made from Sangiovese grapes is generally characterised by a relatively low amount of acylated anthocyanins and a high percentage of ortho-dehydroxylated anthocyanins, which are more susceptible to chemical oxidation than those in red wine made from other grapes (Arapitsas *et al.,* 2012; Bucelli *et al.,* 1992; Lovino *et al.,* 2000). In this regard, the non-acylated anthocyanin monoglucosides, namely Cyanidin 3-O-glucoside, Delphinidin 3-O-glucoside, Peonidin 3-O-glucoside, Malvidin 3-O-glucoside and Petunidin 3-O-glucoside, displayed varying concentrations across areas. Malvidin 3-O-glucoside was the most abundant anthocyanin in all samples, regardless of the production area (Table S1). Sangiovese wines are known for their limited colour stability, which has been attributed to their relatively low levels of stable anthocyanin-derived pigments and a high proportion of monomeric anthocyanins that are more prone to degradation and oxidation over time. However, since the analysed wines were sampled at an early stage, these differences should not be interpreted as the result of aging, but rather as indicators of their potential behaviour during maturation. For example, malvidin-3-O-glucoside, which has been frequently reported as one of the most stable anthocyanins in model wine solutions (Mangani *et al.,* 2011; Mattivi *et al.,* 2006), may contribute to prolonging colour retention over time; therefore, the higher concentration found in wines from the SE area suggests a greater potential for stable colour expression during aging. Hence, colour stability is also advantageous for wine preservation and aging, as it is typically correlated with longevity in wines (Mangani *et al.,* 2011; Mattivi *et al.,* 2006). On the other hand, the NW area showed the lowest Malvidin 3-O-glucoside values and higher Delphinidin and Petunidin values, which are generally associated with cooler-toned colours, often imparting a bluish-violet shade. An additional and critical aspect in evaluating the anthocyanin profiles of Montalcino wines is the ratio between Malvidin and Cyanidin concentrations. This ratio is a reliable index of anthocyanin stability within the wine matrix, as it directly impacts colour retention and longevity (Giannetti *et al.,* 2004). The two southern zones (SE and SW), showed almost identical Malvidin/Cyanidin ratios, averaging around 14. This elevated ratio indicates a potentially robust and stable anthocyanin profile for wines from these regions, as Malvidin is significantly more resistant to oxidative degradation compared to Cyanidin. By contrast, the NE zone displayed a Malvidin/Cyanidin ratio of approximately 11.3, which is moderately lower than the southern zones and may predispose these wines to a higher susceptibility to colour degradation and hue changes as maturation progresses. The most distinct case was observed in the NW region, where the Malvidin/Cyanidin ratio was remarkably lower (5.8). With a lower proportion of Malvidin relative to Cyanidin, NW wines may experience more rapid anthocyanin degradation, leading to potential colour loss and changes in hue as the wine matures (Giannetti *et al.,* 2004).

TABLE 1. Minimum, maximum and average content of total polyphenols, total flavonoids, and total anthocyanins in wines samples from the four areas of Montalcino.

	Total polyphenols				Total flavonoids				Total anthocyanins			
mg/l	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
SE	2411	3257	2700 ^{a}	350	783	1311	960^{b}	204	163	329	224^{a}	65
NW	2051	2949	2580^{b}	330	671	1282	1066^{a}	276	196	285	241^{b}	41
SW	1829	3034	2627^{a}	487	792	1366	1173^{a}	229	162	338	223^{a}	70
NE	2233	2755	2584^{b}	316	921	1364	1164^{a}	176	194	235	212^{b}	15

The mean values are the mean of five wines collected from five wineries per area. Different letters within columns represent statistical significance according to one way ANOVA and post hoc Tuckey test ($p \leq 0.05$)

The flavonol composition of Montalcino wines differed considerably between the different areas, especially regarding quercetin derivatives and Kaempferol content. In the NW area, wines exhibited a high content of Quercetin 3-O-rutinoside. Although flavonol profiling in grape has been widely reported as a varietal marker (Hermosín-Gutiérrez *et al.,* 2011), in the present study only Sangiovese cultivar was investigated. Therefore, the observed differences in flavonol derivatives should rather be attributed to environmental and viticultural factors. Moreover, the higher quercetin levels in the wine may be due to the vinification methods, which involved prolonged skin contact to extract these compounds, and any hydrolysis they may have undergone during subsequent aging. It is important to note that this form of quercetin helps create stable co-pigmentation with anthocyanins. However, Waterhouse *et al.* (Waterhouse *et al.,* 2016) have highlighted an increased tendency for quercetin to precipitate in wines, particularly those based on Sangiovese, due to the hydrolysis of quercetin glycosides over time. As these glycosides break down, they lead to the supersaturation of quercetin aglycones, which then precipitate out, especially in wines that undergo prolonged maceration and extensive aging (Waterhouse *et al.,* 2016). However, in Brunello di Montalcino DOCG, regulatory standards help to mitigate the risk of quercetin deposits in the final bottled product. The mandated minimum of 24 months aging in wood barrels is long enough for the hydrolysis process to substantially reduce glycosylated quercetin levels, and a reduction of over 70 % after approximately 23 months has been shown (Gambuti *et al.,* 2020). Standard cellar practices, such as racking and filtration post-maturation, further assist in preventing visible quercetin deposits, thus maintaining the wine clarity and aligning with consumer expectations for high-quality Brunello di Montalcino (Xiao *et al.,* 2022).

Distinct from the quercetin-rich profile of the NW, the SW region showed a unique presence of Kaempferol, a flavonol not commonly found in other areas. Kaempferol imparts bitterness and can increase overall mouthfeel complexity. The flavanols profiles (Table S3) also showed notable differences. For instance, wines from the SE area were characterised by high levels of catechins and procyanidin B1, both of which contribute to a structured and astringent mouthfeel, likely giving these wines a bold, assertive texture (Rinaldi *et al.,* 2020). Meanwhile, NE samples have elevated levels of procyanidin C1, which is known to increase the wine's structural complexity without adding the same degree of astringency. Since trimers are generally more astringent than dimers, this could imply that NE wines develop a firmer and more persistent astringency, potentially enhancing structural complexity, compared to their SE counterparts. The SW samples showed a more balanced flavanol composition, which might lend a softer and more harmonious mouthfeel.

In terms of phenolic acid content (Table S4), the NW wines were characterised by high levels of Gallic acid, a compound that not only contributes to the wine's bitterness but also increases its structural integrity, particularly in relation to tannin stability (Sterneder *et al.,* 2021). Conversely, SE wines showed lower levels of certain phenolic acids, such as ethyl gallate and caffeoyl tartaric acid, which may affect both the acidity and the potential for a prolonged aging, yielding wines with a possibly more delicate structure in comparison to those from the NW area.

Finally, when examining the non-flavonoid stilbenes, including *trans*-Resveratrol 3-O-glucoside and Piceatannol, a clear differentiation was evident (Table S5). Stilbenes are synthesised by plants, primarily through the phenylalanine pathway, with stilbene synthase being the key enzyme in their biosynthesis. These compounds are produced *de novo* in response to various biotic and abiotic stressors, functioning as phytoalexins, antimicrobial substances that play a crucial role in plant defense mechanisms (Valletta *et al.,* 2021). Since their accumulation is closely related to stress conditions, which may vary across different regions, stilbenes could represent potential markers for vineyard zoning. Moreover, stilbenes are a particularly important class in wine, because they have health-promoting properties (Beaumont *et al.,* 2022) and wine is as one of the primary dietary sources of these compounds in Western countries (Piotrowska *et al.,* 2012). These compounds were more abundant in wines from the SE and NE areas, in particular Epsilon Viniferin, which was detected only in wine from the NE zone. SW wines, on the other hand, contained relatively low levels of stilbenes. These compositional traits could influence the wines' antioxidant capacity and colour preservation during maturation.

Using the data from individual phenols, a PCA was performed to reduce dimensionality while retaining the variability of the data (Figure 2). PC1 explained 57.64 % of the total data variability, while PC2 was associated with 26.79 % for a cumulated variance of 84.43 % (in order to explain 95 % of the total variability, four principal components were necessary). The scores related to the NE area are well segregated in the fourth quadrant and are associated with specific phenols: Epsilon Viniferin, Procyanidin B1, Procyanidin B2, Catechin, Quercetin 3-O-rhamnoside, Kampferol, and Protocatechuic acid. Scores referring to the NW area are segregated between the second and third quadrants and are associated with Gallic acid, gallic acid ethyl ester (Ethyl gallate), t-resveratrol, resveratrol, and caffeoyl tartaric acid. On the other hand, SE and SW, show significant overlap, suggesting similarity in phenolic profiles.

Subsequently, the variables that greatly contributed to segregation and classification of the scores were evaluated and selected based on their VIP score (VIP > 1.00) (Figure 3). VIP scores quantify the importance of each compound in discriminating between the different zones of Montalcino (NE, NW, SE, SW). Epsilon Viniferin clearly emerges as one of the most important, with a VIP score of around 2. Its presence is particularly high in the NW and SW zones, suggesting that it could be a key indicator for wines from these areas. With a VIP score of about 1.8, Procyanidin B3 also plays a significant role in distinguishing between the zones. Its concentration is not only high in the NW wines, but is also relevant in the NE area. Caffeic Acid, with a VIP score of around 1.7, shows high concentrations in the NW wines,

and moderate presence in the SE and SW wines. Quercetin, with a VIP score of about 1.6, is high in the NW wines, and also detectable in the NE and SE ones. Meanwhile, procyanidin Trimer C1 was found to characterise SW and SE samples particularly well (VIP score = 1.5). Among the remaining polyphenols, we can observe a strong influence of epicatechin in the two southern zones (SE and SW) and of gallic acid ethyl ester exclusively in the SW zone. The SE zone is strongly influenced by quercetin rhamnose, piceatannol, and peonidin-3-O-glucoside. These compounds also contributed to the segregation of the samples from the NE zone, albeit to a lesser extent. Compounds such as p-coumaric acid, delphinidin-3-O-glucoside, and quercetin-3-O-rutinoside contributed highly to the segregation of the samples from the NW zone and, to a lesser degree, from the NE zone. Compounds like catechin and protocatechuic acid, on the other hand, have a greater influence on the segregation of all the samples from the NE zone within one quadrant. These results confirm that the multivariate analysis of phenolic profiles can effectively discriminate between wines according to their geographical origin. Similar approaches have been previously reported. For instance, Serrano-Lourido *et al.* (2012) classified Spanish red wines by appellation using phenolic profiles combined with chemometrics. Similarly, Kyraleou *et al.* (2020) discriminated five Greek red grape varieties based on their anthocyanin and proanthocyanidin profiles, and Urvieta *et al.* (2021) demonstrated terroir and vintage discrimination of Malbec wines across multiple sites in Mendoza, Argentina, based on phenolic composition. All these results indicate the strong influence of climate and terroir on phenolic biosynthesis. Environmental conditions, such as temperature, sunlight exposure, and water availability, are known to affect both the overall accumulation of polyphenols and the ratio between individual anthocyanins (Koundouras, 2018). Therefore, the observed differences between the Montalcino subzones are likely the result of complex interactions between terroir-related environmental conditions and the intrinsic genetic determinants of Sangiovese.

Additionally, cluster analysis was applied to the chromatographic data as a complementary chemometric approach (Figure S1). The two-way dendrogram clearly explains this segregation into groups. When combined using a multivariate approach, the polyphenol values can be seen to have contributed to the separation of the samples from the various areas into three large clusters. One cluster contains samples from the NW zone, and another those from the NE area, indicating very distinct phenolic profiles. Meanwhile, the third cluster comprises samples from two southern zones suggesting high similarity between their phenolic profiles, as has been previously highlighted.

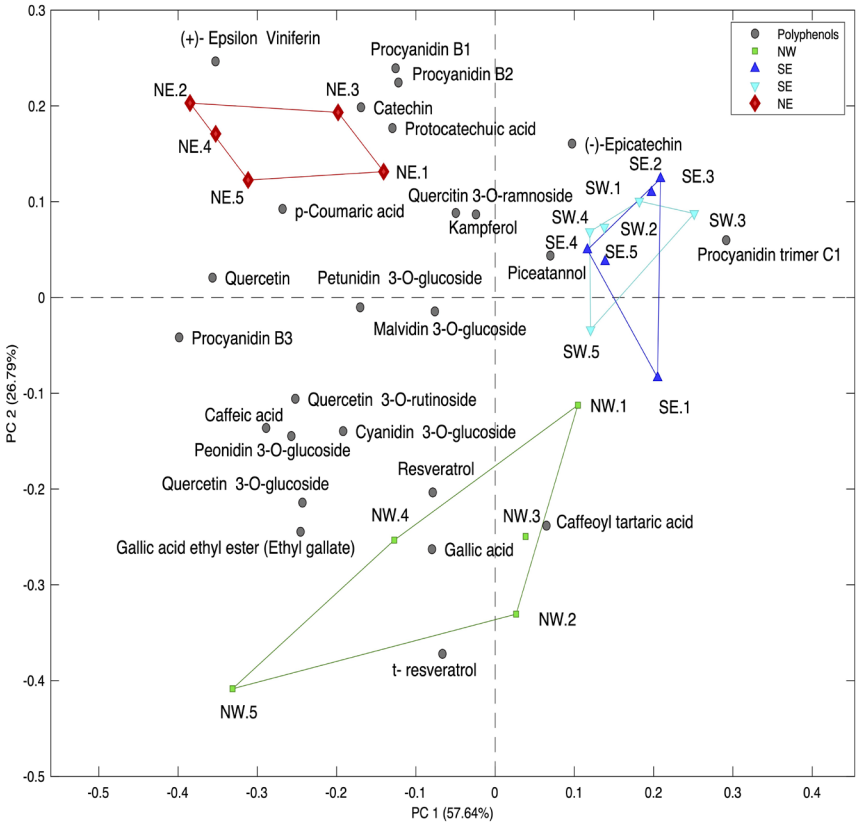


FIGURE 2. Biplot (PC1 vs PC2) of the PCA obtained from the phenolic data acquired by HPLC-DAD. Wine production areas: south-east (SE), north-west (NW), south-west (SW) and north-east (NE). The lines connecting the classes represent the confidence ellipse between the five replicates.

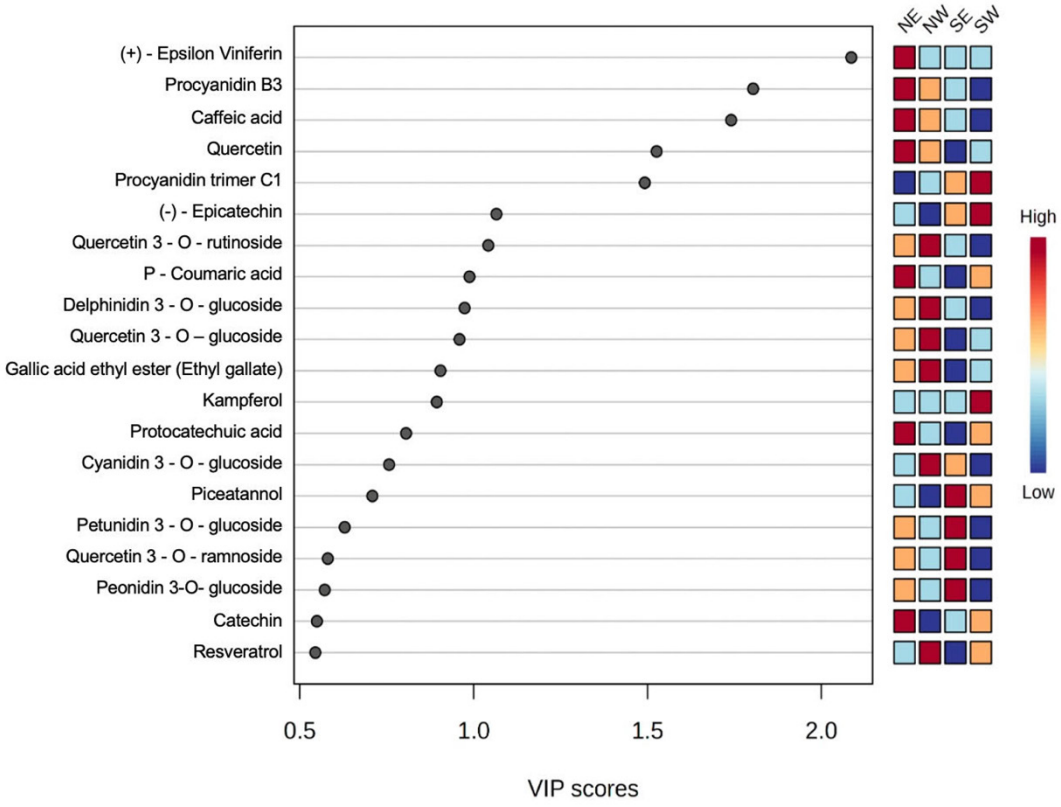


FIGURE 3. Effect of variables (loadings, HPLC polyphenols -DAD) on discrimination of PCA pattern recognition performed on chromatographic acquisitions. The influences are evaluated as a variable importance projection (VIP) generated by each variable and estimated on the basis of an effectiveness threshold (equal to 1).

2. NIR spectroscopy

NIR spectra were acquired from the different wines. NIR spectroscopy, through the absorption of electromagnetic radiation associated with overtone and combination vibrations of molecular bonds, allows the characterisation of wine composition (Nicolai *et al.,* 2007).

A filtering of first derivative of absorbance units was carried out on the raw spectra, followed by a PLS-DA computation. The model that was applied is graphically represented as a scatterplot in Figure 4. The first latent variable (LV1) explains 56.22 % of the variance, while the second (LV2) the 16.50 %, for a cumulative explanation of 72.77 %. Seven principal components were needed in order to minimise the residual statistical error below 5 % (95 % of the residual variance explained). Each area is clearly located in a specific quadrant, suggesting significant differences between them in terms of spectral profiles: the NE zone is entirely segregated in the first quadrant, the SW in the second, the NW zone in the third and the SE zone in the fourth.

Figure 5 shows the variable importance in projection (VIP) related to spectral bands which are responsible for the segregation of the scores belonging to the different Montalcino areas. Specific bands contributed highly to differentiating the different areas. For instance, bands between 1350 nm and 1400 nm differentiated all four production areas. The bands between 1540-1600 nm, 1680-1720 nm, and 1800-1880 nm contributed highly to discriminating between the NE and SE areas. Meanwhile, the SW zone shows VIP > 1 for bands between 1100-1400 nm and 1550-1700 nm, and the NW area shows VIP > 1 for the bands between 1100 and 1200 nm and 1580-1630 nm. The observed VIPs can provide important information concerning the impact of spectral bands on the observed sample clustering. Specifically, absorbance bands between 1350 nm and 1400 nm can be attributed to the overtone and combination bands of C-H, N-H, and O-H stretching vibrations, and therefore be related to distinct phenolic profiles as well as carbohydrates fraction. The range of around 1600 nm has been reported to be linked to condensed tannins (Cozzolino *et al.,* 2008; Ferrer-Gallego *et al.,* 2020). Moreover, C–H bonds display absorbance bands that are due to their stretching at third (928 and 940 nm), second (1148 nm), and first overtones (1620 and 1652 nm) (Osborne *et al.,* 1993; Bokobza *et al.,* 1998). Lastly, absorbances between 1100 and 1300 nm correspond to a combination band involving symmetric and antisymmetric stretching vibrations of O-H, as well as a combination band related to the second overtone of C–H aromatic vibrations and the third overtone of C–H vibrations (Bokobza *et al.,* 1998).

Most of the research regarding the application of NIR technology in wine analysis and specifically focusing on zoning has emerged over the past decade. In all the studies

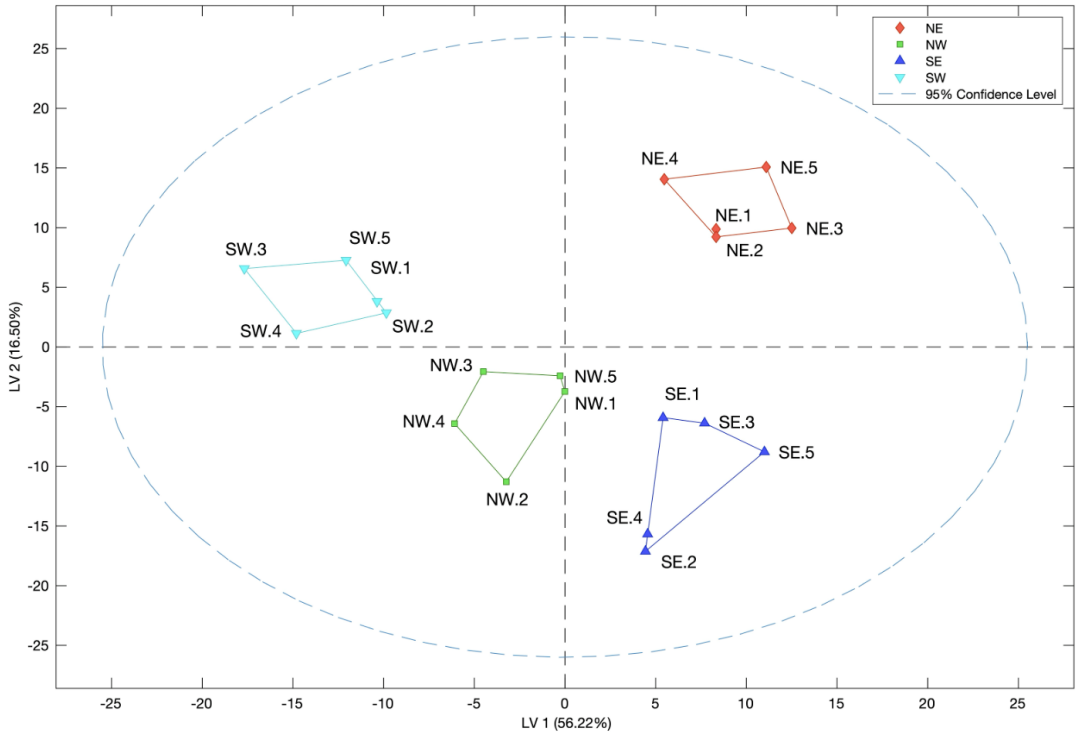


FIGURE 4. Score plot (LV1 vs. LV2) of PLS-DA obtained from the data acquired via NIR-AOTF. The spectra have been transformed into absorbance. Wine production areas: south-east (SE), north-west (NW), south-west (SW) and north-east (NE). Lines connecting the classes represent the confidence ellipse between replicates.

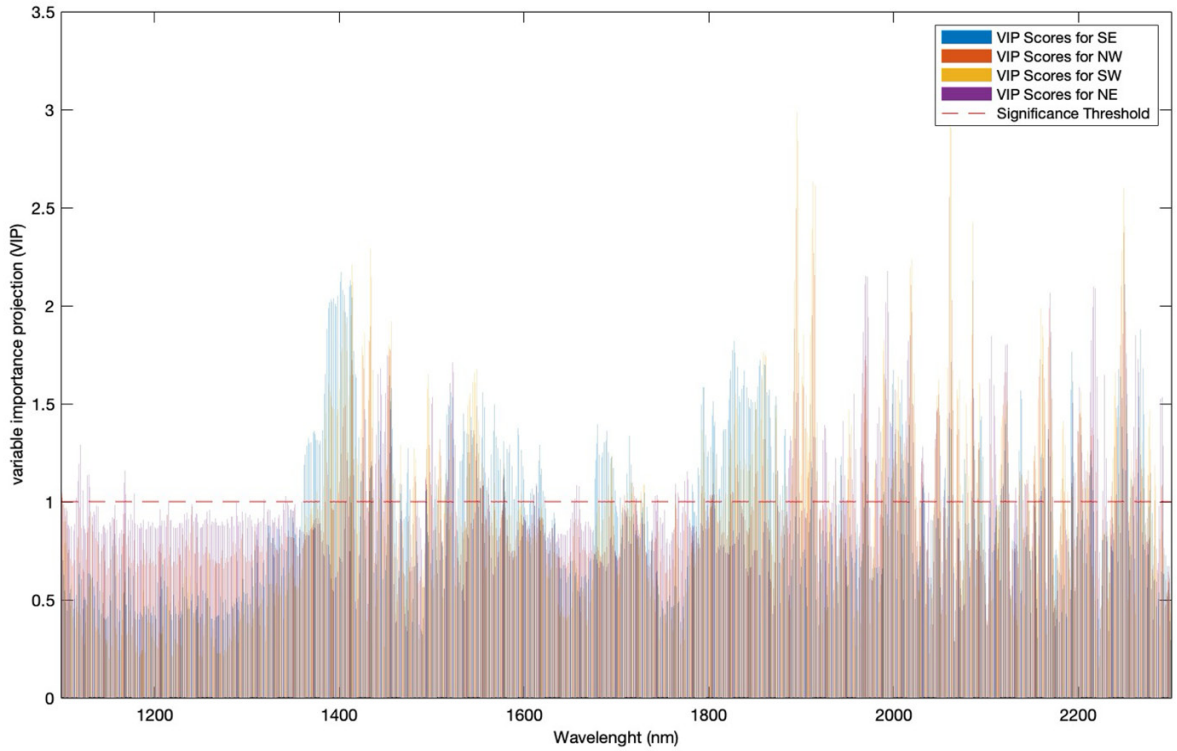


FIGURE 5. Effect of variables (loadings, wavelength (nm) NIR-AOTF) on the pattern recognition discrimination of PLS-DA performed on the acquisitions of the NIR samples. The influences are evaluated as a projection of the VIP (variable importance projection) generated by each variable (wavelength) and appreciated on the basis of an efficacy threshold (equal to 1). Wine production areas: south-east (SE), north-west (NW), south-west (SW) and north-east (NE).

employing vibrational spectroscopy, researchers have consistently observed similar absorbance patterns across the spectrum. However, due to the intricate interplay of absorption mechanisms and overlapping bands, establishing a direct link between certain molecules (such as phenolic compounds) and the size of these bands remains challenging (Ferrer-Gallego *et al.,* 2020). Despite this, the significant bands responsible for identifying compounds in wine, such as water, sugar, and polyphenol, remain consistent. Our findings confirm that NIR technology can effectively discriminate between different geographical zones within a production area. As confirmed by the confusion matrix generated by the PLS-DA model built using NIR spectra (Table S6), the various samples were correctly assigned to their respective areas in both the calibration and prediction computations. This ability to distinguish zones is significant, because it enables the identification of subtle variations in wine composition due to geographic and pedoclimatic differences. This aptitude is particularly valuable for enhancing the quality control and characterisation of wines from distinct production zones, even by rapid and non-destructive tools, as already demonstrated in previous studies (Cozzolino *et al.,* 2003; Yu *et al.,* 2017; Liu *et al*., 2006).

3. Aromatic profile

The HS GC-MS approach was used to identify a total of 59 compounds belonging to the alcohol, aldehyde, ketone, ester, organic acid, and terpenoid classes (Table S7), which were used to build a PCA model (Figure 6). By means of three principal components, the model describes 83.09 % of the variability (PC1 41.22, PC2 31.08 and PC3 10.07, respectively). Five principal components were needed to reach 95 % of the explained variability (PC4 7.45 and PC5 5.27). The volatile composition of wines was significantly influenced by geographic origin. For instance, notable differences were identified between the NE and NW areas, as well as between these northern areas and the southern ones. By contrast, the SE and SW areas show a lot of overlap and a clear discrimination between them is not possible, therefore indicating a consistent similarity in their aromatic profiles. In more detail, the NE area was characterised by specific compounds, such as phenylethyl alcohol (2-PE), Butanedioc acid, propanoic acid, 2,3, Butanedione and 2 heptanone 4 methyl. All these compounds are generally produced during fermentation but are associated with different aromas (Tapia *et al.,* 2022). For instance, 2-PE is known for its pleasant rose-like aroma and Butanedioc acid is often associated with a sweet aroma (Hu *et al.,* 2019). On the other hand, propanoic acid can confer an unpleasant sweaty odour, especially when it reaches a certain concentration (Chen *et al.,* 2023). Similarly, 2,3-Butanedione is known for imparting a buttery aroma to wine, which can be desirable in small amounts but become an off-flavor at higher concentrations (Li *et al.,* 2017). NW area was characterised by octanol, nonanal, 2-nonenal and 2 propanol 2 methyl, among others. Octanol is known to contribute to mouldy aromas in wine. The health status of grapes can affect octanol levels: healthier grapes tend to have lower concentrations of mould-related compounds, including octanol; on the other hand, nonanal is a powerful volatile aldehyde with a strong fatty-floral odour (Porcaro *et al.,* 1963). The presence of the other two key volatiles in the NW area is attributable to the fermentation and aging processes. Hence, 2-Methyl-1-propanol is a higher alcohol produced by yeast metabolism (Lee *et al.,* 2019) which in moderate concentrations contributes positively to wine bouquet by giving complexity, and in overly high concentrations can be undesirable (Šehović *et al.,* 2007). 2-Nonenal is an aldehyde that contributes to the oxidative flavour profile of wine (Mayr *et al.,* 2015; Cullere *et al.,* 2007). It is part of a group of compounds known as (E)-2-alkenals, which are associated with flavour deterioration in wines, and it tends to increase with exposure to oxygen during aging (Cullere *et al.,* 2007). Lastly, the southern areas (SE and SW) were associated with several primary grape-derived compounds, as well as with others related to fermentation. For instance, 1-hexanol is typically present in certain wine-grapes varieties and contributes to green, grassy and floral notes (Fabani *et al.,* 2013). 1-Hexanol, produced via the LOX pathway (Rubio-Bretón *et al.,* 2019; Ferrandino *et al.,* 2012), is a pre-fermentative C6 alcohol that typically originates from the oxidative degradation of linoleic acid released from the phospholipid membranes of grape cells. Moreover, cadinene, calamenene and farnesene belong to the class of sesquiterpenes, which is a class of cultivar-related terpenoids. These compounds significantly contribute to flavour complexity, varietal character and particularly to woody, black pepper and green apple scents (Li *et al.,* 2020). Meanwhile, ethyl caproate - known for its apple-like aroma - is an important volatile found in the study area (Chen *et al.,* 2016) that is produced during fermentation by *Saccharomyces cerevisiae*. Therefore, its presence is mostly influenced by fermentation conditions (Qin *et al.,* 2022). Similarly, ethyl caprate is influenced by yeast activity and fermentation methods. Its presence enhances fruity notes and contributes to the wine's complexity and appeal (Lu *et al.,* 2020). Other volatiles are instead attributable to aging processes (*i.e*., butyrolactone and 2- heptanal). The content of butyrolactone is affected by the aging process (Elliott *et al.,* 2005) and it is generally associated with cheesy, burnt sugar, and caramel notes (Simonato *et al.,* 2019). Meanwhile, 2-Heptanal has been identified as a compound that significantly contributes to the oxidative flavour, increases with aging and it is often undesirable (Mayr *et al.,* 2015).

Wine aroma is a complex and multifaceted aspect of wine quality, influenced by a variety of factors and compounds. It is primarily determined by volatile compounds originating from grapes, fermentation processes, and aging. Therefore, it is not surprising to observe large differences in aroma between different areas. Hence, climate, including temperature and solar radiation, strongly affects the content of aromatic compounds in grapes, which in turn determine the final wine aromas. These climatic variations contribute to the unique volatile profiles of wines from different production zones (Xu *et al.,* 2017; de Souza Nascimento *et al.,* 2018). Moreover, *terroir*, encompassing topography, soil and

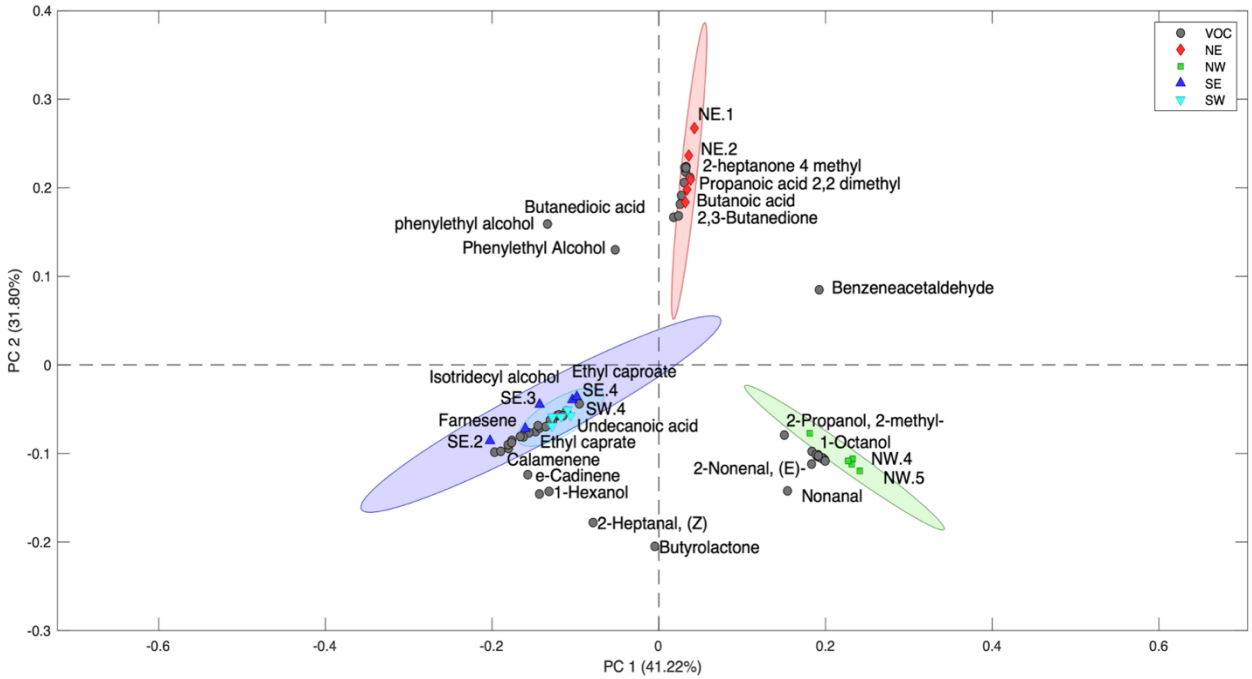


FIGURE 6. Biplot (PC1 vs PC2) of sample scores and variable loads obtained by PCA performed on VOCs detected in wines from different areas. Wine production areas: south-east (SE), north-west (NW), south-west (SW) and north-east (NE).

climate, influences the levels of grape metabolites related to wine organoleptic properties (Koundouras *et al.,* 2018). The interaction of these environmental factors with viticultural condition, as well as with winemaking practices, fermentation and aging conditions, plays a crucial role in defining the final volatile profiles of wines from different zones. Lastly, sub-regional differences in wine aroma can be attributed to different soil characteristics, which affect the volatile and sensory profiles of wines (Lola *et al.,* 2023). Even though the results obtained suggest that there are environmental differences between certain areas (i.e., NE and NW) and that others (SW and SE) are similar, the impact of *terroir* on volatile compounds cannot be ignored. Therefore, a more detailed analysis of soil characteristics and vineyard management, for example, would be beneficial to better understand how these factors influence profiles of wines from the different Montalcino areas.

4. E-nose

The aromatic fingerprint of wines was also analysed using an QMB-based E-nose. Figures 7 and 8 show the biplot and VIP scores respectively of the PLS-DA model built from the data obtained from the E-nose measurements. The model describes approximately 84 % of the variability of the first two latent variables (LV1 72.39 % and LV2 10.84 %), while four LVs were needed to explain 95 % of the variability. Interestingly, the spatial distribution of the samples in the biplot perfectly reflect what was observed in the volatile profile. Hence, three different clusters can be clearly observed. The first cluster includes wine samples from the NE area, which appear to be homogeneously segregated due to the influence of QMB2 (cobalt-functionalised sensor). The second well-segregated area comprises the NW area, which is strongly correlated with QMB10, a copper functionalised microbalance. The segregation of the NE and NW areas is described by the first latent variable, and QMB1, QMB3, QMB4, QMB6, QMB7, QMB8, QMB9, and QMB12 are spatially arranged between the two areas. By contrast, the wines from the two southern zones, SW and SE, tend to segregate jointly along the second latent variable between quadrants 1 and 2. This suggests that the aromatic profiles of wines from these two southern zones are very similar and distinctive, as confirmed by the head space analysis and VOC identification. The frequency variations of the quartz microbalances integrated in the E-nose device gives information on the amount and structures of molecules adsorbed onto their surfaces (Muñoz-Castells *et al.,* 2024). When molecules adhere to the coated layer above the surfaces of the QMBs, there is a shift in their oscillation frequency. This shift is directly proportional to the amount of absorbed mass. QMBs are typically coated with different materials. Each sensor, therefore, has an individual and unique response based on its sensitivity and selectivity, which depends on the specific functionalisation (Capuano *et al.,* 2020). The molecules on the sensor surface exhibit varying degrees of affinity for specific classes of aromatic compounds, and the intrinsic response of each sensor is influenced by the chemical structure and concentration of volatile compounds (VanDeventer *et al.,* 2001). Hence, upon evaluating the VIPs, it becomes evident that both areas are influenced by cobalt-functionalised (QMB5) and copper-functionalised (QMB10), despite the spatial distance between them, indicating a balanced influence. Previous studies showed that QMB5 correlates with volatile acids and ethanol, whereas QMB10 interacts preferentially with polar volatile compounds such

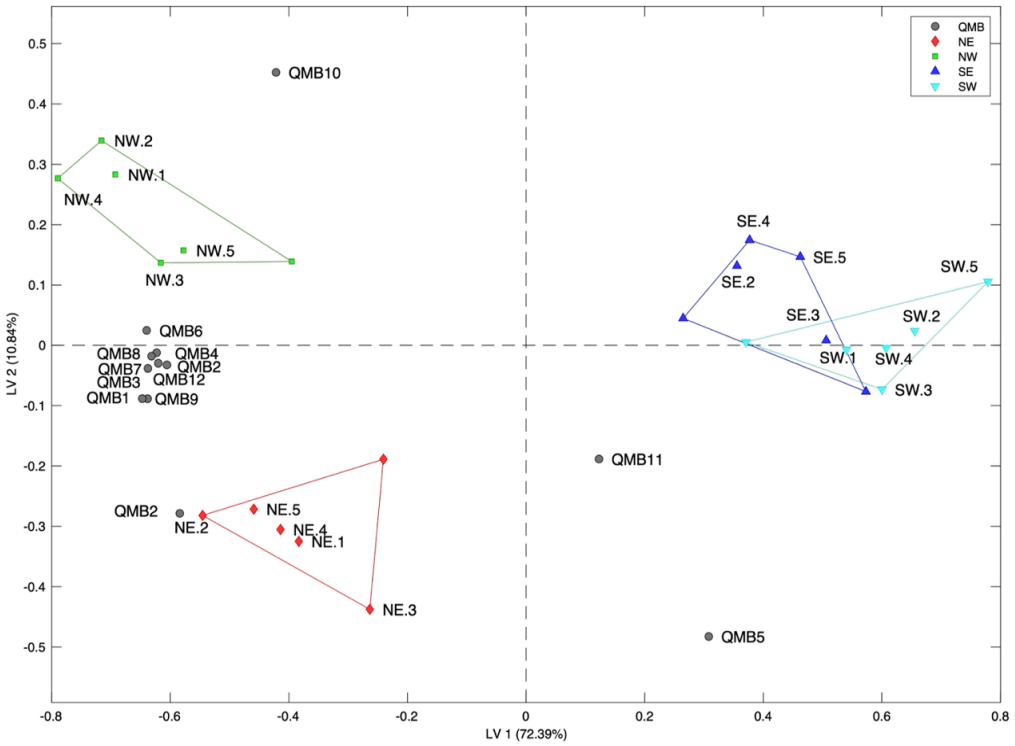


FIGURE 7. Score plot of latent variables (LV1 versus LV2) of the partial least square discriminant analysis model built with pre-treated E-nose data of the wines. Wine production areas: south east (SE), north west (NW), south west (SW) and north east (NE).

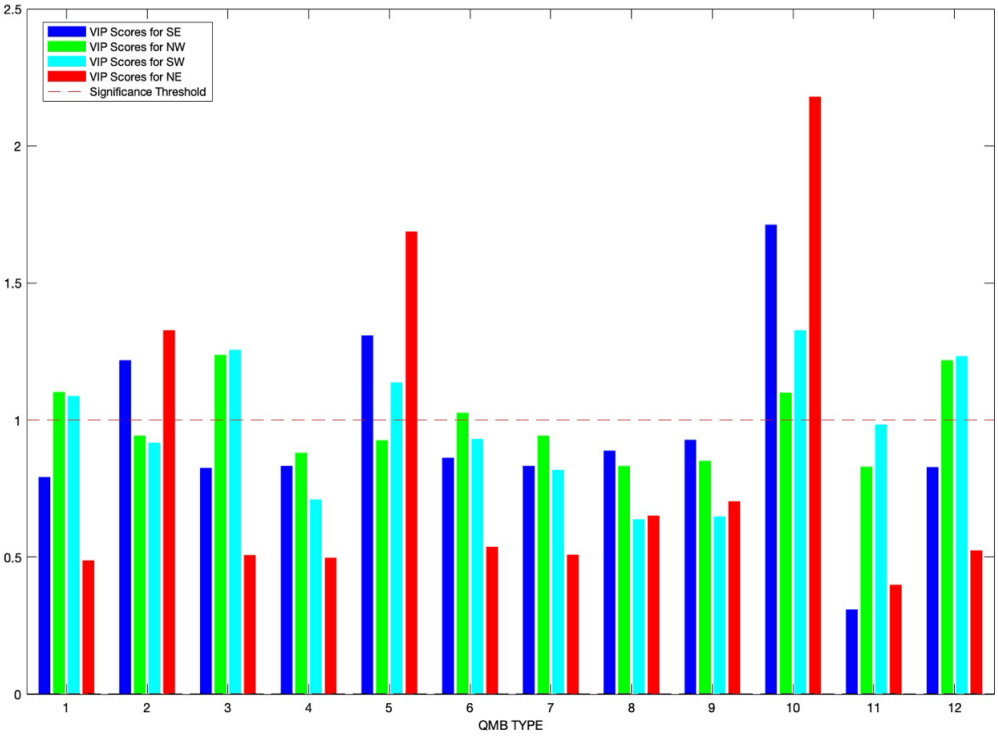


FIGURE 8. Effect of variables (loadings, QMB sensors) on the pattern recognition discrimination of the partial least square discriminant analysis performed on the acquisitions of the electronic nose headspaces samples of different wines. The influences are evaluated as a projection of the variables of importance in projection (VIP) generated by each variable (QMBs) and appreciated on the basis of an efficacy threshold (equal to 1).

as alcohols and aldehydes (Capuano *et al.,* 2020). Since these volatiles are known to be modulated by both viticultural and winemaking conditions, their influence on QMB5 and QMB10 responses may explain the high discriminant power of these sensors and further support the impact of terroir on wine volatile composition. Additionally, QMB1 strongly affects the two western areas, NW and SW. This sensor, functionalised with Mn-TPP (tetraporphyrin), tends to form bonds with alkanes, such as Nonadecane (Capuano *et al.,* 2020; VanDeventer *et al.,* 2001; Nan *et al.,* 2019).

Our findings using the electronic nose align perfectly with those observed in the GC-MS analysis, thus confirming the e-nose's capability to accurately discriminate between changes in the aromatic profile and potentially between different production areas. Similar applications of E-nose devices have successfully differentiated wines by geographical origin. For example, Marques *et al.* (2024) demonstrated the ability of QMB-based E-nose combined with chemometric modelling to differentiate wine produced in different Portugal regions. Similarly, E-noses coupled multivariate data analysis techniques such as Discriminating Factor Analysis (DFA) have been successfully applied to for accurate discrimination of wine samples based on origin (Martì *et al.,* 2004) This performance can be confirmed by the confusion matrix of the PLSDA model (Table S8). Hence, in calibration phase, the different samples are correctly assigned to their respective areas. In prediction, the robustness of the model slightly falls, being a SE sample assigned to SW class. However, the model maintains very good prediction capability, with an estimated error of 5 %.

CONCLUSIONS

In this study, we explored terroir-driven differences between phenolic and aromatic profiles of Sangiovese wines destined to become Brunello di Montalcino DOCG in order to determine whether the wines can be differentiated according to their sub-geographic origins. Sangiovese, the cornerstone of Tuscany's viticulture, serves as the exclusive grape variety in Brunello di Montalcino, a wine that has close ties with the land and the cultural identity of the Montalcino area. This historical bond, coupled with the region's stringent DOCG standards, provides a robust framework for evaluating whether and how sub-regional distinctions within Montalcino contribute to a more refined "zoning" of the production area. Zoning, in this case, aims to strengthen the link between wine and territory, increasing wine identity and communicating the uniqueness of each sub-region to consumers. Even though a real and definitive zoning of a larger number of wine samples (also referred to as a more extended time window) would need to be considered, our findings highlight some important sub-area differences that reflect Montalcino terroir's diversity. The analysis of the phenolic profiles reveals slight yet meaningful differences across the four production zones, suggesting that each area may impart specific traits to the wines. For instance, SE wines exhibited a high concentration of Malvidin 3-O-glucoside, known for enhancing colour stability and longevity, while NW wines, with a lower Malvidin/Cyanidin ratio, could be subject to more rapid colour change. Variations in phenolic profiles across the regions contribute to distinct structural and mouthfeel characteristics, and reflect the influence of local climatic and pedoclimatic conditions on phenolic composition. The aromatic profile analysis further highlighted terroir-driven distinctions. For example, NE wines were enriched with phenylethyl alcohol and 2,3-butanedione, adding rose and buttery notes, while NW wines displayed higher levels of octanol and nonenal, volatile compounds associated with oxidative aromas. By contrast, wines from the SE and SW regions were characterised by esters and terpenoids, such as ethyl caproate and cadinene, which enhance fruity and peppery aromas. NIR and E-nose assessments revealed well-defined groupings of the wines based on their geographical origin, with NE and NW wines exhibiting distinct profiles and SE and SW wines showing considerable overlap, indicating shared characteristics. These results suggest that zoning could effectively differentiate the Montalcino wine regions based on measurable phenolic and aromatic attributes, thus contributing to an elevated identity and marketability for Brunello di Montalcino wines. However, this study remains a preliminary differentiation of Brunello di Montalcino wines across sub-regions due to the absence of detailed analyses on soil composition and specific climate data, and the fact that the vintage effect and winemaking practices were not taken into account, which are critical factors in fully understanding terroir influences.

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