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Scale effect of terroir under three contrasting vintages in the Chianti Classico area (Tuscany, Italy)

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ABSTRACT

In viticulture, terroir is a concept used to explain the specific combination and interaction of natural and human factors that provides distinctive characteristics to the wine. The role of soil and geology on wine characteristics is debated and sometimes considered less important than either climate or the human component.

The present study, performed on one of the largest farms of the "Chianti Classico" wine district (Tuscany, Italy), focused on the effect of terroir on wine characteristics using two different zoning scales. At a broader scale, called macro-terroir (MT), the experimental vineyards were selected based on lithology, soilscape, morphology, and mesoclimate. Each vineyard was then subdivided at a detailed scale into two homogeneous zones for soil features, the Basic Terroir Units or Unité Terroir de Base (UTB). The study was conducted during three different vintages (2012, '13 and '14), in vineyards located in four different MT, which are representative of large parts of the Chianti Classico wine district. The vineyards were surveyed by proximal sensors, namely electromagnetic induction sensor (EMI) and gamma-ray spectroscopy to characterize soil spatial variability and to define two homogeneous areas (UTB) of about 2 ha in each MT. The UTB differed for some soil features, mainly texture, gravel content, soil depth, available water capacity, and internal drainage. The weather for the three vintages was very different e during the growing season, which was very dry and hot in 2012, moderately wet and warm in 2013 and chilly and very wet in 2014. Grape harvest, wine-making and six-month ageing were carried out separately for the different UTB, using the same methodology. Mixed-design analysis of the variance of several must and wine features demonstrated that MT played the major role on must pH, as well as total acidity, glycerine content and colour intensity of the wine. The climate of the vintage played a stronger role than MT on the content of must malic acid, as well as polyphenols, anthocyanins and dry extract of the wine. Blind wine sensory analysis performed for all vintages showed significant differences between wines from the different UTB, in particular for colour intensity and wine aroma, but the differences between UTB within each MT were not stable over the three contrasting vintages, being less pronounced in the most humid vintage (summer 2014).

This study demonstrates that characteristics of pedo-geological landscapes can be used for a wine district zoning, while a more detailed soil mapping, leading to UTB identification, is needed for differentiating particular wine characteristics.

1. Introduction

The concept of "terroir" has long been used in viticulture to describe the relationships between the sensory attributes of wine and the geographical territory from which it is derived (Vaudour, 2002; Deloire et al., 2005). The terroir distinction has progressively gained relevance in wine marketing as a tool to endorse the quality of wines and improve their competitiveness and profitability on the international markets. Probably more than many other foods and beverages, wine has a strong identity and a tight connection with its place of origin (Salette et al., 1998; Bucelli et al., 2011; Costantini et al., 2016).

To date, the terroir concept is not easily understood and remains one of the most debated issues in the world of wine, because of the large variety of interacting natural and human factors, on which there is not always agreement. These factors include climate, soil, topography, grapevine cultivar, viticultural and oenological practices, which together create unique and distinctive characteristics in the wine from a given place that is perceived and recognizable by consumers and

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experts (Fischer et al., 2016; Costantini et al., 2016; Barham, 2003; Vaudour et al., 2015; Wilson, 1998). According to the definition adopted by the International Organization of Vine and Wine (OIV), the viti-vinicultural terroir refers to "an area in which collective knowledge of the interactions between the identifiable physical and biological environment and applied viti-vinicultural practices develops, providing distinctive characteristics for the products originating from this area" (OIV, 2010).

Beside the human factor, which plays the most important role through viticultural and oenological practices, the natural factors that are most important in the expression of terroir may vary depending on the spatial scale. At a "regional scale", macroclimate in interaction with the grapevine cultivar is likely to be most important (Jones et al., 2005). At a "within-region" and "wine district" scale, the interaction between mesoclimate, topography and geology might be the dominant factors driving grapevine performance and grape peculiarities (Nicholas et al., 2011; Priori et al., 2014b; Ramos et al., 2015). Topography greatly affects mesoclimate by altitude, proximity to large water bodies, aspect, and slope. It is well known that during grape ripening, the spatial variability of day and night temperatures plays a very important role in separating wine producing areas characterized by different grape maturation, aroma, and colouration (Tonietto and Carbonneau, 2004). The role of geology on wine peculiarities is much more debated. While many authors (Vaudour, 2002; Van Leeuwen and Seguin, 2006; Costantini et al., 2012; Bonfante et al., 2015) assert that vineyard geology contributes significantly to wine peculiarities, other authors consider the effects of soil and bedrock on grape and wine negligible (Matthews, 2016).

Although vineyard geology is widely hypothesized to contribute significantly to wine typicity, there is still little scientifically-based knowledge on how this connection is established and which specific geological parameters are involved. Some significant examples are the relationship of Chablis wines with Kimmeridgian limestone, or that of Beaujolais wines with granite, which along with many others are taken as a crucial for the expression of wine typicality (Van Leeuwen and Seguin, 2006).

Matthews (2016) asserts that the word "terroir", interpreted as geology and soil associated, is often abused and not preceded by scientific discoveries of soil- and rocks-derived flavours or characteristics of the wine. He also writes that "grapevines have next to no interaction with rocks" (Matthews, 2016) which supports Maltman (2008), who wrote that a direct rock geochemical influence on wine is undemonstrated and scientifically impossible. The author disapproves of the use of direct connection between wine flavours and rocks, like "minerality, rocky flavour", "quartz taste", and "smell of graphite", the latter for wines produced in schists with graphite in Priorat (Maltman, 2008). On the other hand, he also affirms that rock and soil features can indirectly influence the bio-chemical pathway of elements during grape growing and vinification, and then wine peculiarities. Characteristic isotopic speciation and transfer can been followed from bedrock to soil, vine, grape, and wine, thus allowing wine origin to be traced at a very detailed scale (Braschi et al., 2018).

Certainly, the role of geology might be expressed indirectly. The bedrock geology determines the relief and the landforms of an area, and is a key factor in soil genesis. The nature of the bedrock, along with its physical status (colour, hardness, compaction, presence of planes of weakness) and degree of weathering, greatly influence soil physical and hydrological properties, which influence root development and water uptake. Moreover, the bedrock geochemistry affects soil pH, nutrient supply, and balance, which are crucial for vine growth and grape composition (Kodur, 2011; Retallack and Burns, 2016).

However, the relationship between soil properties and the underlying bedrock may not always be so clear. For instance, soils can develop from allochthonous parent material, such as aeolian sediments, colluvial depositions, or human transported materials (Dazzi et al., 2009). In other cases, the relationship can be broken by erosion (Martínez-Casasnovas and Concepción Ramos, 2009) or land preparation activities for vineyard planting, including levelling, bedrock crashing, and deep ploughing. These activities can reduce soil depth, disturb the natural soil profile, and can increase the short-range spatial variability of the soil across a vineyard (Costantini et al., 2015). Therefore, at the farm or "within-vineyard" scale, soil characteristics are credited as major terroir components (Bramley et al., 2011a, 2011b; Tardaguila et al., 2011; Priori et al., 2013a, 2013b). Soil physical properties, such as texture, structure, internal drainage, and soil depth, influence soil temperature, soil/water relationships, and root development, which subsequently influences water and chemical nutrition of the vine (Morlat and Bodin, 2006). Chemical nutrition is critical for grapevine development and berry production, but there is often a weak or no relationship between the soil nutrient status and wine quality, due to factors regulating plant nutrient uptake, including soil nutrient dynamics and availability, soil water content, vine rooting patterns and antagonism between nutrients (Garcia et al., 2001; Mackenzie and Christ, 2005). More attention is given to soil water status and water uptake conditions, which are confirmed as key factors of terroir (Costantini et al., 2013; Marciniak et al., 2013; Bonfante et al., 2015). High grape quality, especially for red wine, is often associated with mild water deficit, which in rainfed vineyards is related to a complex interaction between climate (rainfall, evapotranspiration), soil hydrology (water holding capacity, internal drainage) and the density and distribution of vine roots (Bonfante et al., 2011; Costantini et al., 2013; Deloire et al., 2005; Dry, 2016; Marciniak et al., 2013; Brillante et al., 2016).

A recent approach to investigate and manage soil spatial variability in vineyards consists of mapping homogeneous management zones using proximal and remote sensing methods, which provide increased resolution and accuracy of soil spatial characterization, while reducing the sampling costs, and improving management of wine quality in relation to soil features (Acevedo-Opazo et al., 2008; Taylor et al., 2009; Bramley et al., 2011a, 2011b; Bonfante et al., 2015; Vaudour et al., 2017; Tardaguila et al., 2017). Some authors refer to homogeneous management zones as the "Basic Terroir Units" or "Unité Terroir de Base" (UTB), to underline the concept that each of them represent the smallest useful area for vineyard management, in which the natural factors (soil, geology, climate) are homogeneous and have uniform effect on vine biology and wine quality (Deloire et al., 2005). Key questions in this approach, also reported by Bramley (2016a, 2016b), include: does variation in soil properties have a functional impact on grape and wine composition? At what scale are these effects expressed? How stable are these effects across vintages characterized by contrasting climatic conditions?

The present study was conducted in one of the largest and most renowned wineries in the "Chianti Classico" district (Tuscany, Italy), the Barone Ricasoli farm. The objective of the research is to evaluate the effect of terroir on wine quality at two different zoning scales: i) the "macro-terroir" (MT) level, as defined according to geology, soilscapes, morphology and climate, and ii) the UTB level, based on the division of each MT into homogeneous sub-zones according to soil proximal sensing survey and soil physical-hydrological properties (texture, gravel content, depth, available water capacity).

2. Materials and methods

2.1. Study variety and area

The grapevine cultivar studied was *Sangiovese*, the most important for "Chianti Classico" and other high quality wines of Central Italy, such as "Brunello di Montalcino", "Vino Nobile di Montepulciano" and "Morellino di Scansano". The *Sangiovese cv*. can express a wide variety of wine peculiarities, due to its high responsiveness to the environmental factors (Bucelli et al., 2004; Dalla Marta et al., 2010; Ducci, 2013; Mattii et al., 2005; Scalabrelli et al., 2001). Moreover, it is very

Fig. 1. Main soilscapes of the Chianti Classico DOCG area, as reported by Pollini et al. (2014) and Amato and Valletta (2017, modified). SAND: hills and low mountains on feldspathic sandstone (Macigno formation); CALC: hills on clayey-calcareous flysch (Monte Morello formation); MS: hills on flysches mainly made by marls, shales and calcarenites; MAR_s: low hills on marine sandy deposits; MAR_c: low hills and plains on marine clayey and silty deposits.

sensitive to water stress and it is identified as an anisohydric cultivar (Poni et al., 2007). Anisohydric and near-anisohydric cultivars, like Sangiovese, Sirah, etc., continue to transpire even when soil water content diminishes because of poorer stomatal adjustment capacity than isohydric and near-isohydric cultivars like Montepulciano, Cabernet Sauvignon, and Grenache (Schultz, 2003; Palliotti et al., 2014). This strategy makes the anisohydric plants less water-efficient and more affected by soil water shortage (Poni et al., 2007).

A 3-year project was carried out on the “Barone Ricasoli” estate, one of the widest and oldest farms in the Chianti Classico wine district, where the Chianti wine “formula” was formalized in the year 1872 (Simone et al., 2015). The 1200 ha farm is in the northern part of the province of Siena with 230 ha dedicated to viticulture. The vineyards, planted at elevations that span from 180 to 490 m a.s.l., with different slopes and aspects, display characteristic features of the typical terroir of the Chianti Classico district (Fig. 1). The farm includes the four main geological units of the Chianti Classico district, which are: i) the Ligurian Unit: a succession of clayey-carbonate sedimentary rocks of Cretaceous-Eocene period; ii) the upper part of Tuscan unit: a succession of clay-calcareous-marls, covered by a thick layer of feldspathic sandstone (Macigno Formation) of Oligocene period; iii) the marine deposits: silty-clay and sandy-gravelly marine deposits of Pliocene period; iv) the fluvial terraces: fluvial deposits of different textural composition and different period, from Pliocene (ancient terraces) to Holocene. In this area, the Ligurian Units and the upper part of Tuscan unit are generally on the top of the hills (400–600 m a.s.l.) or along slope at high-medium elevation (300–500 m a.s.l.), whereas marine deposits and fluvial terraces are situated beneath 300–350 m a.s.l. From a morphological point of view, the slopes of Ligurian Units and Tuscan Units are usually steeper than the others, because of the nature of hard bedrock (limestone, sandstone and marls).

For this work, we defined as “macro-terroir” (MT) a large area, characterized by similar lithology, morphology, and climate, which delimits a soilscape. A soilscape is defined as an area which groups soils having functional relationships and similar pedogenesis and that can be represented at 1:250,000 scale (Finke et al., 1998). We defined as “Basic Terroir Units” (or Unité Terroir de Base, UTB; Morlat, 2001) subareas within MT of about 2 ha in size, characterized by homogenous soil features (texture, stoniness, soil depth, available water capacity, etc.). The UTB size was based upon the capacity of the cellar tanks (9 tons), which is a suitable amount to produce a commercial wine brand (around 10.000 bottles).

A total of seven vineyards were selected (Fig. 2), across 4 MT showing the following characteristics:

- ***Calcareous flysch*** (***CALC***): MT developed on clayey-calcareous rocks (Monte Morello Formation), situated on regular slopes between

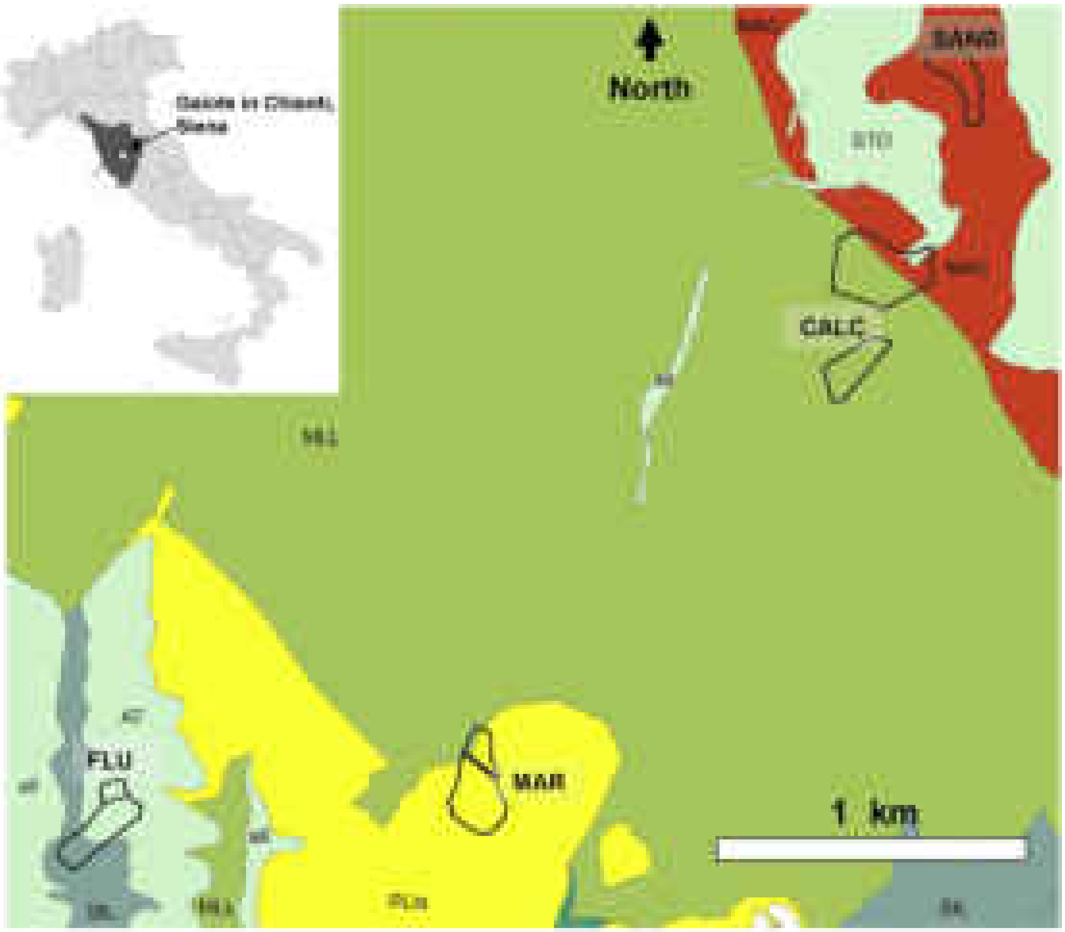

Fig. 2. Experimental vineyards plotted on geological map 1:10.000. Legend: all-recent alluvial deposits; AT-alluvial terraces; PLIs: marine sands with conglomerate lenses; SIL: shales of Ligurian Unit; MLL: clay-calcareous flysch of Ligurian Unit; MAC: feldspathic sandstone; STO: limestones, marls and shales of Tuscan Unit.

400 and 450 m a.s.l. According to the maps of soilscapes reported by Pollini et al., 2014, this formation covers around 35% of the total area of Chianti Classico DOCG. The regional soil map (scale 1:250,000, Gardin and Vinci, 2006) reports a soilscape formed by the association of shallow and very gravelly soils, with loam, silty clay loam or clay loam texture, usually very rich in calcium carbonates, classified as *Calcaric Cambisols*, *Calcaric Leptosols* and *Calcaric Regosols*.

- ***Sandstone*** (***SAND***): MT characterized by poorly weathered soils developed on feldspathic sandstone (Macigno del Chianti Formation), situated on regular slope or high-plains of the hills between 430 and 470 m a.s.l. This formation covers around 25% of the total area of Chianti Classico DOCG (Priori et al., 2013a, 2013b). The soils are characterized by sandy or loamy-sandy texture, usually high stoniness and very low content or absence of calcium carbonate ($< 1\%$). The soils of this macro-terroir are classified as *Eutric Regosols*, *Eutric Cambisols* and *Cutanic Luvisols* (Gardin and Vinci, 2006).

- ***Marine deposits*** (***MAR***): MT developed on marine sands and gravelly-sands of early Pliocene period, situated on slopes around 300–350 m a.s.l. Such MT is very common in central Tuscany, where deep sandy deposits accumulated in a marine basin during the Pliocene period (4.8–4.2 Ma ago) (Martini et al., 2011). These deposits cover around 18% of the total area of the Chianti Classico DOCG (Priori et al., 2013a, 2013b). The soils of this MT can have different degree of pedogenesis, due to the balance between erosion and stability during the Quaternary period. The soil types span from *Calcaric Regosols*, *Calcaric Arenosols*, *Calcaric Cambisols*, and in some cases, *Cutanic Luvisols* (Gardin and Vinci, 2006). The texture is variable between sandy-loam to clay-loam and the calcium carbonate content is usually medium (around 15%).

- ***Fluvial terraces*** (***FLUV***): MT situated at lower elevation than the others (250–320 m a.s.l.) and characterized by soils developed on ancient fluvial deposits (Pliocene-Quaternary). This MT is not reported in Fig. 1, since the fluvial terraces are discontinuous in the study area. Although this MT is not as widespread as the previous, several ancient fluvial terraces are present in the Chianti area. In the ancient fluvial terraces of central Tuscany, the regional soil map shows soils with different weathering and pedogenetic development, usually calcareous and with loamy and loamy clay texture, varying from *Calcaric Fluvisols*, *Calcaric Cambisols*, *Eutric Cambisols*, and *Cutanic Luvisols* (Gardin and Vinci, 2006).

Only one important MT of the Chianti Classico DOCG, which covers around 15% of the total area of the district (MS, Fig. 1) and is characterized by soils developed on sequences (flysches) of marls, shales and calcarenites, was not investigated during this work.

The studied MT are not only present in the Chianti area, but also in other territories of the Tuscany region. In the Province of Siena, where other wines are produced from the same *Sangiovese* variety, two MT reported in this paper, namely CALC and SAND, correspond to the "Natural Terroir Units" n.6: loamy soils with frequent stoniness, high calcium carbonate developed on calcareous flysches; and n.9: sandy-loamy soils with frequent stoniness, low calcium carbonate, developed on sedimentary rocks rich in sand (arenites) (Priori et al., 2014b).

Climatic data were acquired in each MT by weather stations during the three years of the project (2012–2014). Mean daily temperature, minimum and maximum daily temperature, as well as daily precipitation were collected. A modified Winkler index (WI_{mod}) was calculated following the method of Amerine and Winkler (1944), changing the end of the time range from 31st October to 30th September. The modification was necessary because Sangiovese grape harvest in this area always occurs between the second half of September and the beginning of October. CALC and SAND were comparable for average temperature and WI_{mod}, whereas MAR and FLUV showed slightly lower mean temperatures. Night temperatures were lower in the area closer to the valley bottom (FLUV and MAR) than at higher altitude (CALC and SAND). The "Cool night index" (CI, Tonietto and Carbonneau, 2004) showed temperate nights in CALC and SAND (14.1–14.7 °C), and cool nights in MAR (12.9–13.8 °C) and FLUV (11.9–12.6 °C). All the experimental vineyards had comparable summer precipitation (P7/8), calculated from 1st of July to 31th of August.

All the experimental vineyards were cultivated with the *Sangiovese* cultivar. The age of the vineyards was similar (12–16 years) and the trellis system was the simple spurred cordon with vertical shoot positioning. The vigour was managed with moderate shoot topping and the soil was tilled during early summer. Grapevine density was similar, ranging between 2 × 0.75 m (CALC and SAND) and 2.1 × 0.8 m (MAR and FLUV), which means 6200–6600 vines/ha. The experimental blocks received the same viticultural treatments during the growing season. None of the vineyards were irrigated, like most of DOCG vineyards from Chianti Classico and other wine districts from central Italy.

2.2. Mapping Basic Terroir Units (UTB)

The experimental vineyards were surveyed by soil proximal sensing to obtain high-detail maps of soil spatial variability and to delimit Basic Terroir Units (or Unitè Terroir de Base, UTB) within each MT.

The proximal sensors used were: i) EM38-Mk2 electromagnetic induction sensor (Geonics Ltd., Ontario, Canada) and ii) "The Mole", gamma-ray spectroradiometer (Soil Company, The Netherlands). EM38-Mk2 measures the soil apparent electrical conductivity (ECa) across two depth ranges of 0–75 and 0–150 cm, approximately (McNeill, 1990). The ECa measurements are influenced by several soil properties, including clay content (Sudduth et al., 2005; Morari et al., 2009), gravel content (Morari et al., 2009; Priori et al., 2013a), soil moisture and water availability (Cousin et al., 2009; Zhu et al., 2010), bulk density (Taylor et al., 2009), salinity (Triantafilis et al., 2000), and soil depth (Priori et al., 2013b).

"The Mole" spectroradiometer continuously measures the gamma-ray natural emission coming from the first 30–40 cm of the soil and rocks, through a Cesium Iodide scintillator crystal (van Egmond et al., 2008). Proximal gamma-radiometrics has been used to survey topsoil features, such as texture (Pikki et al., 2013; Priori et al., 2014a), gravel content (Priori et al., 2014a), potassium (Castrignanò et al., 2012), and organic carbon (Dierke and Werban, 2013, Priori et al., 2016). For the survey, the gamma-ray spectroradiometer was mounted on the back of a tractor, whereas EM38-Mk2 was inserted in a non-metallic chariot, which was pulled by the same tractor through a 2 m long shaft. The latter is needed to avoid the influence of metallic mass of the tractor on ECa measurements. The sensors were supplied with GPS and rugged PC for data-logging. A proximal soil survey was carried out in April 2012, when the soil moisture was between 10 and 20% in volume. Soil sensing was performed continuously around every 8 vine rows, and the data were interpolated across the whole vineyard areas using ordinary kriging (OK). The parameters of OK, namely lag size, number of lags, and maximum range were selected in order to minimize the estimation error (mean kriging variance, σ_{krig}). Two clusters in each MT were delimited according to the k-means clustering (Fig. 3). The variables used for clustering were: apparent electrical conductivity ECa_1 and ECa_2, total count of gamma-ray (TC), as well as slope and aspect, obtained by a digital elevation model with a detail of 10 m. Because of the manual grape-harvest, the cluster areas were simplified to delineate the UTB based upon a compromise between the results of clustering and the farm needs (Fig. 2).

A minimum size of 1.5–2 ha was adopted to obtain around 9 tons of grapes from each UTB, which was the volume of grapes needed by the winery to fill in their steel tanks. Each MT was then subdivided into two UTB, for a total of 8 UTB. Small areas, characterized by deep and fertile soils due to the downslope accumulation, waterlogging, or exceptional soil erosion, were excluded from the delineation of UTB. The significant differences of the soil proximal sensing data between the couples of UTB within each MT were investigated following the method of Taylor et al. (2007). The authors proposed that two classes have sufficient variation if:

$$Y_{Class1} - Y_{Class2} \geq \left(\sqrt{\sigma^2_{krig}} \times 1.96\right) \times 2 \tag{1}$$

where Y_{Class1} and Y_{Class2} is the mean of the selected soil variable in UTB1 and 2.

2.3. Soil analysis and monitoring

Within each UTB, three representative soil profiles of about 1.5 m were dug. The location of digging followed the variability captured by the soil survey with proximal sensors (see below). Soil profile description followed the national and international guidelines for soil description (Costantini, 2007; Jahn et al., 2006) and classification according to the Word Reference Base for Soil Resources (WRB; IUSS Working Group WRB, 2014). Soil stoniness was estimated in the field using a reference frame of 30 × 30 cm.

Soil samples were collected from the several genetic horizons of each soil profile. The samples were air-dried, sieved to 2.0 mm and analysed for physical and chemical properties. Soil texture was determined by the X-ray/sedimentation method, using a Micromeritics Sedigraph III analyser (Andrenelli et al., 2013).

Total organic C (TOC) and total N (N_{tot}) were measured by dry combustion with a ThermoFlash 2000 CN soil analyser, after removal of carbonates by HCl 10%. The total equivalent $CaCO_3$ content was calculated from the difference between the total C measured by dry combustion in the untreated soil (mineral C + organic C) and in the HCl-treated soil (organic C) (Sequi and De Nobili, 2000). The active lime was determined according to the Drouineau method, based on a 2 h treatment with 0.1 M ammonium oxalate and following back-titration with 0.1 M $KMnO_4$ (Loeppert and Suarez, 1996). Soil pH was measured potentiometrically in a 1:2.5 soil–water suspension. Electrical conductivity was measured in a 1:2 soil–water filtered extract after 2 h shaking and overnight standing. Soil cation exchange capacity (CEC) and exchange bases were analysed with the $BaCl_2$-triethanolamine (pH 8.2) method. The amounts of Ca, Mg, K and Na in the extracts were quantified by flame atomic absorption spectrometry, using an Agilent SpectrAA 220FS spectrometer (Gessa and Ciavatta, 2000). The soil water retention was determined using a pressure plate apparatus (Klute, 1986). Water retention at field capacity (FC) and wilting point (WP) (−33 and −1500 kPa matric potential, respectively) were measured on the < 2 mm soil fraction. The values of moisture content at FC and WP were corrected for gravel content according to Gardner (1986).

2.4. Wine characteristics

The grapes from each UTB were carried to the farm winery, where they were separately vinified in stainless steel tanks, using the same oenological techniques, as follows: i) crushing and destemming; ii) addition of SO_2 (15 mg·L^{-1}) and dry selected yeast (200 mg·L^{-1}); iii) 15-day maceration at controlled temperature punching the cap down six times a day until 3 Babo units; iv) the wines were poured after a soft pressing into 5 hectolitres oak barrel (tonneaux) for a 6-months ageing. All these operations were repeated every vintage of the trial (2012-'13-'14). The grape musts were analysed for sugar content, pH and malic acid.

Seven months after grape-harvest, the wines were analysed to assess the alcohol content, total polyphenols and anthocyanins, total acidity,

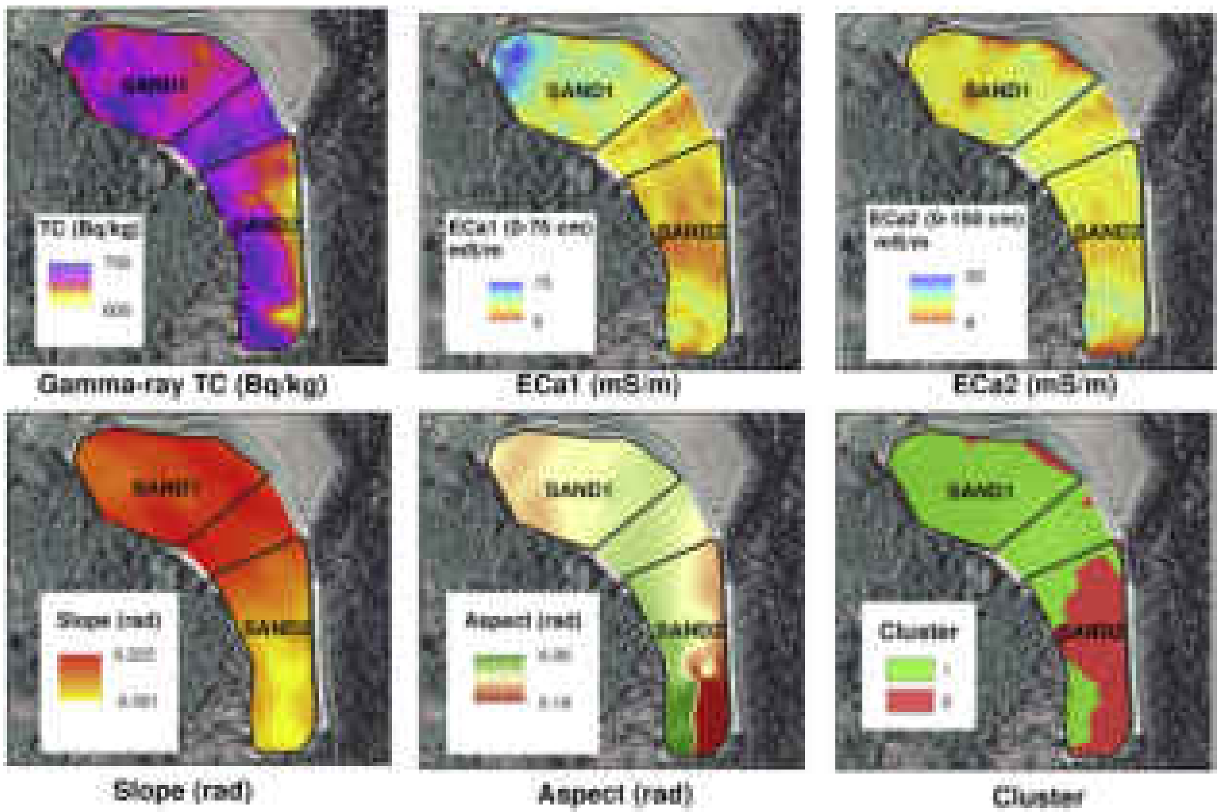

Fig. 3. Example of UTB mapping in the vineyard of SAND MT. In the first row, the maps obtained by the proximal sensing: gamma-ray total counts (TC), apparent electrical conductivity of 0–75 cm and 0–150 cm. In the second row, the maps obtained by DEM: slope and aspect, and the two clusters obtained by k-means clustering using the previous maps after value standardization. The polygons SAND1 and SAND2 showed the UTB used for the grape harvest.

dry extract, glycerine, and colour intensity. Malic acid, titratable acidity, polyphenols, anthocyanins, net dry extract and glycerine were determined by FTIR (Fourier Transform Infrared Spectroscopy), using a wine analyser WineScan FT (FOSS, Denmark) (Bevin et al., 2006). Colour intensity (CI) and hue (Hue) were measured according to Glories (1984) using an AGILENT (USA) 8453 DAD spectrophotometer.

Moreover, the wines were evaluated by a panel of 10 wine tasters through a "blind tasting". Sensory analysis was performed to assess differences among the wines, therefore the evaluation method was mainly comparative. The wine tasters gave a score, ranging from 1 to 10 to several wine parameters, giving score 10 to the wine which best expressed the parameter. The sensory parameters were: colour intensity, flavour intensity and balance, structure, acidity, astringency, and persistence. A score was also given to the overall evaluation of the wine. In addition, the tasters indicated their feeling about the wine in terms of aroma typology (fruity, floral, spicy, herbaceous), using 0-absent, 1-scarce, 2-medium, and 3-strong.

2.5. Statistical analysis

Several statistical approaches were used to investigate the effects of vintage, MT and UTB on oenological parameters and wine tasting scores. Effect of the spatial variability of mesoclimate throughout MT was investigated by non-parametric correlation (Spearman's ranks) between WI_{mod}, CI, P7/8 and wine features.

Significant differences among groups have been tested by one-way ANOVA and Fisher's LSD test, using the vintage, the MT, and the UTB as grouping factor. Fisher's LSD test determines the significant differences between group means in an analysis of variance. Parametric Student's *t*-test and non-parametric Mann-Whitney *U* test were run to verify statistical difference between the couples of UTB within a MT. To verify the interactions between the effects vintage, MT, and UTB, mixed design models were adopted for each must and wine variable, using vintage as random factor, MT as fixed factor and UTB nested in MT (hierarchical nested ANOVA). The same methods were used to analyse the scores of wine tasting.

A multivariate analysis of the oenological data was also carried out using principal component analysis (PCA), considering as active variables alcohol content, total wine acidity, total polyphenols, total anthocyanins, dry extract, glycerine, and colour intensity index. Pedological and climatic variables were also plotted in the factor loadings graph (Fig. 5, left) as supplementary variables. These are not included in the calculation of PCA, but they are plotted in the factor loadings graph according to the correlation with the PCA factors. The factor score graph (Fig. 5, right) demonstrates the statistical separation among MT using a multivariate approach.

3. Results

3.1. Basic Terroir Unit (UTB)

The apparent electrical conductivity (ECa) measured at 0–75 cm (ECa_1) and 0–150 cm (ECa_2) depths, ranged between 5 and 45 $mS{\cdot}m^{-1}$, generally showing higher values in ECa_2 (Table 1). On average, the lowest ECa values (around 5 $mS{\cdot}m^{-1}$) were observed in SAND2 ($ECa_1 = 5.2\ mS{\cdot}m^{-1}$) and SAND1 ($ECa_1 = 8.7\ mS{\cdot}m^{-1}$), both characterized by sandy soils and SAND2 by high stoniness (> 35%, Table 2). On average, the ECa of CALC, MAR and FLUV were similar and vary between a mean of about 16 $mS{\cdot}m^{-1}$ (FLUV2) and about 33 $mS{\cdot}m^{-1}$ (MAR1). According to Eq. (1), ECa_1 showed significant differences between the clusters within every MT (Table 1), whereas ECa_2 showed no significant differences between the clusters of SAND.

Gamma-ray spectroscopy provided very different total counts (TC) according to the MT (Table 1). The mean TC value of soils on calcareous

Table 1
Mean values of the variables used for clustering and within each UTB, as simplified for grape harvest. In bold, the significant differences, following the method of mean kriging variance (σ_{krig}) (Taylor et al., 2007). *: aspect is reported in radiant (rad) and main direction (S: South, SE: South East, SW: South West).

MT	Cluster/UTB	Area	ECa_1	ECa_2	TC	Slope	Aspect*
		ha	$mS \cdot m^{-1}$		$Bq \cdot kg^{-1}$	%	rad (direction)
CALC	σ_{krig}	–	*1.6*	*1.2*	*17*	n.d.	n.d.
	Cluster1	2.1	**17.7**	**24.0**	297	12.0	4.1 (SW)
	Cluster2	2.4	**24.1**	**29.2**	343	8.9	3.5 (SW)
	CALC1	2.2	20.5	28.2	316	13.6	3.8 (SW)
	CALC2	2.3	22.3	26.5	333	9.3	3.9 (SW)
SAND	σ_{krig}	–	*0.6*	*0.6*	*17*	n.d.	n.d.
	Cluster1	2.6	**8.7**	13.4	671	15.6	3.8 (SW)
	Cluster2	1.3	**5.2**	11.6	657	6.9	3.9 (SW)
	SAND1	2.0	**8.2**	12.4	669	14.0	3.7 (SW)
	SAND2	1.9	**5.7**	12.2	666	8.8	3.6 (SW)
MAR	σ_{krig}	–	*2.4*	*1.7*	*12*	n.d.	n.d.
	Cluster1	2.5	**32.7**	**30.8**	**408**	11.1	3.0 (S)
	Cluster2	2.6	**21.7**	**22.3**	**361**	18.4	2.2 (SE)
	MAR1	2.3	**32.9**	**31.0**	**410**	12.8	2.9 (S)
	MAR2	2.8	**23.4**	**23.4**	**358**	17.6	2.2 (SE)
FLUV	σ_{krig}	–	*0.7*	*0.7*	*12*	n.d.	n.d.
	Cluster1	1.9	**28.0**	**32.8**	**485**	10.9	2.9 (S)
	Cluster2	1.9	**15.6**	**22.8**	**379**	16.7	3.6 (SW)
	FLUV1	2.0	**22.5**	**28.5**	443	11.3	3.1 (S)
	FLUV2	1.8	**19.0**	**25.6**	404	19.5	3.6 (SW)

flysch (CALC) was 317 ± 40 $Bq \cdot kg^{-1}$, and the differences between CALC1 and CALC2 were not significant. The TC value of soils on feldspathic sandstone (SAND) was on average 667 ± 21 $Bq \cdot kg^{-1}$, with no significant differences between SAND1 and SAND2. The only significant difference of TC values between the couple of clusters was calculated in MAR, and varied between 358 ± 59 $Bq \cdot kg^{-1}$ (MAR2) and 410 ± 35 $Bq \cdot kg^{-1}$ (MAR1). In FLUV, no significant difference was observed, although TC varied between 404 ± 62 $Bq \cdot kg^{-1}$ (FLUV2) and 443 ± 65 $Bq \cdot kg^{-1}$ (FLUV1).

Radionuclide concentration (data not reported) followed the same trend of TC, although the ratio between $^{40}K/^{238}U$ and $^{40}K/^{232}Th$ was slightly higher in the soils of feldspathic sandstone. The high gamma-ray emission and ^{40}K radionuclide concentration in these soils was probably due to the high percentage of potassium rich minerals, like muscovite and feldspars, which are very frequent in such kind of sandstone (Macigno del Chianti formation). Within of a same parent material, the spatial variability of gamma-ray TC and radionuclides concentration is mainly influenced by the topsoil texture and surface stoniness. The relationships between gamma-ray spectroscopy and soil features in these vineyards are reported in detail by a previous work (Priori et al., 2014a).

The 8 UTB represented areas very suitable for high quality grape and characterized by a certain internal homogeneity in terms of soil features, hydrology and microclimate. The geometrical simplification of the cluster areas in UTB did not show any significant loss of statistical differences between groups, with the only exception of CALC (Table 1). The soil profiles of CALC1 and CALC2 were all classified as *Skeletic Calcaric Cambisol* (*Loamic*) (IUSS Working Group WRB, 2014) and characterized by clayey loamy texture, high stoniness and calcium carbonate, as well as moderately low water permeability (K_{sat}). CALC1 profiles showed significant lower sand content, total calcium carbonate and slightly higher TOC and exchangeable potassium (K) than CALC2 (Table 2).

The soil profiles of SAND1 and SAND2 were classified as *Eutric Cambisol* (*Arenic*) and *Skeletic Eutric Cambisol* (*Arenic*), respectively. These soils showed sandy loam texture, high stoniness and permeability, as well as very low organic matter and nitrogen content. SAND1 showed significant lower stoniness and K content, but higher available water capacity (AWC) than SAND2 (Table 2).

MAR1 and MAR2 showed the best differentiation between the UTB of the MT, and their soils were classified as *Calcaric Cambisols* (*Loamic*, *Colluvic*) and *Calcaric Cambisol* (*Arenic*), respectively (IUSS Working Group WRB, 2014). MAR1 was a reddish-brown, deep, well preserved and strongly structured soil. The texture was variable between loam and clay-loam, with variable content of rounded cobbles and pebbles of heterogeneous lithology. Calcium carbonate was low (< 5%), TOC and N_{tot} were medium and pH was neutral or sub-alkaline (7.5–8.3). MAR2 was the soil situated in the areas of the slopes more sensitive to erosion, therefore the soil was shallower, less preserved and structured than MAR1. The colour was pale brown or yellowish and the texture was sandy or sandy-loam, with a general high content of cobbles and pebbles. Calcium carbonate was moderate (10–20%), whereas pH was sub-alkaline. This soil was also characterized by a low content of organic matter and nitrogen.

The UTB FLUV1 and FLUV2 were situated on two different landforms: the first on gentle slope at the top of the hill (ancient terrace surface), the second one along the slope connecting the ancient to the recent fluvial terraces. Both soils showed loamy or clay-loamy texture, poor soil structure, moderate calcium carbonate (8–19%) and very low content of organic matter and nitrogen. FLUV1 was deeper and showed significant lower sand, calcium carbonate, stoniness, TOC, nitrogen and water permeability than FLUV2. Both the UTB soils showed sub-alkaline pH (8.1–8.4) and were classified as *Calcaric Cambisol* (*Loamic*) (IUSS Working Group WRB, 2014).

3.2. Weather of the three vintages

The weather was variable over the three years of study, as reported in Fig. 4, with the following trends during the grapevine growing season (1st April–30th September):

Table 2
Means and standard deviations of soil features analysed in each UTB (3 profiles and, only for clay, sand, and stoniness, 6 augerings), calculated as average values on soil horizons (0–90 cm) with the only exceptions of TOC and Ntot, measured in Ap horizons (about 0–30 cm). [1]: total calcium carbonate; [2]: total organic carbon; [3]: total nitrogen; [4]: exchangeable potassium, [5]: available water capacity; [6]: saturated hydraulic conductivity. In bold, significant differences between the UTB couples of MT, calculated by Student's *t*-test ($p < 0.05$).

UTB	Clay	Sand	$CaCO_3$[1]	Stoniness	TOC[2]	Ntot[3]	K[4]	AWC[5]	Ksat[6]
	$(g \cdot 100\, g^{-1})$			$(m^2 \cdot m^{-2})$	$(g \cdot kg^{-1})$		$(mg \cdot kg^{-1})$	$(mm \cdot m^{-1})$	$(mm \cdot h^{-1})$
CALC1	36.0 ± 3.9	**16.5 ± 2.7**	**38.7 ± 9.1**	30.8 ± 10.9	**6.6 ± 0.1**	0.7 ± 0.1	**132 ± 12**	114 ± 27	2.1 ± 0.4
CALC2	33.6 ± 5.8	**21.6 ± 1.2**	**57.0 ± 1.7**	36.2 ± 10.5	**5.4 ± 0.1**	0.8 ± 0.1	**107 ± 7**	94 ± 10	2.3 ± 1.0
SAND1	9.8 ± 3.5	59.8 ± 5.5	1.7 ± 0.6	**19.2 ± 2.7**	4.4 ± 0.6	0.4 ± 0.1	**74 ± 4**	**113 ± 27**	19.7 ± 5.9
SAND2	10.0 ± 2.7	61.0 ± 5.2	2.6 ± 0.6	**36.5 ± 6.6**	3.9 ± 1.2	0.3 ± 0.1	**170 ± 23**	**64 ± 11**	22.8 ± 14.7
MAR1	**35.3 ± 5.9**	**33.5 ± 6.8**	**13.3 ± 3.2**	**8.1 ± 3.7**	**8.4 ± 1.1**	**0.9 ± 0.1**	149 ± 67	**139 ± 3**	7.5 ± 7.7
MAR2	**19.2 ± 4.3**	**51.3 ± 5.8**	**26.7 ± 2.1**	**21.8 ± 10.6**	**5.8 ± 2.1**	**0.6 ± 0.2**	86 ± 30	**103 ± 21**	11.6 ± 2.6
FLUV1	31.5 ± 3.8	**31.4 ± 5.1**	**12.3 ± 6.4**	**7.0 ± 3.4**	**3.3 ± 1.1**	**0.4 ± 0.1**	126 ± 28	79 ± 8	**2.5 ± 0.6**
FLUV2	25.5 ± 7.9	**39.8 ± 6.0**	**28.3 ± 8.4**	**27.2 ± 10.2**	**6.1 ± 1.9**	**0.7 ± 0.2**	100 ± 36	67 ± 19	**9.1 ± 1.3**

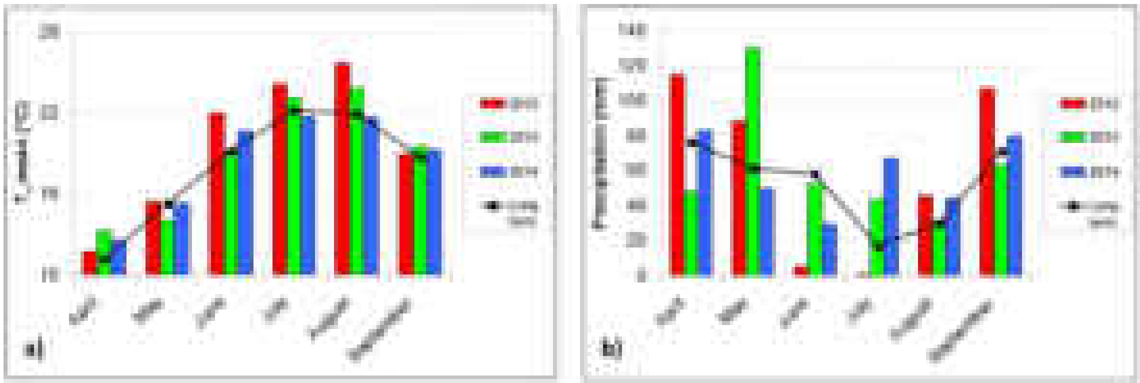

Fig. 4. Monthly mean temperature (a) and precipitation (b) during the grapevine growing season (1st of April–30th of September) of the three vintages. Black line showed the long term data (20 years) of the area.

Table 3
Mean elevation of the four MT and the climatic data of the three years. [1]: WI_{mod}, Winkler index modified (calculated according Amerine and Winkler, 1944, using the time range from 1st April to 30th September, instead than 31st of October); [2]: CI: Cool night Index (Tonietto and Carbonneau, 2004); P7/8, Summer precipitation during grape veraison period, measured from 1st of July to 31th August.

MT	h	2012			2013			2014		
		WI_{mod}[1]	CNI[2]	P7/8[3]	WI_{mod}[1]	CNI[2]	P7/8[3]	WI_{mod}[1]	CNI[2]	P7/8[3]
	(m a.s.l.)	Σ°C	°C	(mm)	Σ°C	°C	(mm)	Σ°C	°C	(mm)
CALC	435	1897	14.3	58	1790	14.3	52	1523	14.7	136
SAND	480	1878	14.3	58	1799	14.1	52	1514	14.4	136
MAR	325	1761	13.8	42	1567	12.9	70	1511	13.4	127
FLUV	315	1677	12.6	40	1474	11.9	67	1456	12.6	127

- 2012: mean temperatures were close to long-term average in spring, but much higher in June, July and August. Mean daily temperature was higher than 22 °C from the middle of June to the beginning of September. The modified Winkler Index (WI_{mod}) resulted about 1800 °C on average (Table 3). Summer was extremely dry, with no precipitation between 12th of June and 30th of August. The 31st of August and 1st of September were characterized by two intense rainstorms (around 50 mm each).
- 2013: April was warm, but with a sudden temperature decrease in the second half of May. Summer was warm and long, with the only exception of a short period of temperature decrease at the end of June. WI_{mod} was about 150 °C lower in 2013 than 2012. Precipitation was higher than the average in July, with 6 rainy events (> 3 mm) well distributed between June to August. September was slightly warmer and drier than the average.
- 2014: Mean temperature was slightly lower than average during most of the summer, with the only exception being a short warmer period at the beginning of June. WI_{mod} was around 1500 °C. Precipitation frequency was very high and above the average for summer, with 11 rainy days between July and August and 6 in September.

The MT CALC and SAND, which were located near the top of the hills with south aspect, showed the highest heat sum (WI_{mod}, Table 3), whereas the MT FLUV showed the lowest WI_{mod} and CI, because of the thermic inversion induced by the river valley. Precipitation in the different MT were comparable (Table 3).

3.3. Must and wine analytical features

The contrasting climate conditions between the experimental years resulted in significant vintage-to-vintage differences in the grape and wine quality. The harvest date was when the grape in each vintage reached average values of 220 $g \cdot L^{-1}$ of sugars, corresponding to the following dates: 23–25 September 2012, 1–3 October 2013, 29 September–3 October 2014.

The mild and humid summer of 2014 provided grape musts with higher acidity (pH 3.19 on average) and malic acid, while vintage 2012, characterized by high temperature and scarce precipitation during summer, produced grape musts with low malic acid and wines with the lowest content of polyphenols and anthocyanins. Summer 2013, which can be considered representative of a good vintage for Sangiovese cultivar, provided, on average, the highest values of polyphenols, anthocyanins, and dry extract in the wine.

Spatial variation of WI_{mod}, CI, and P7/8 did not show any statistical correlations with the must and wine parameters in 2012. In 2013 CI was correlated with must sugar and wine anthocyanins (rs 0.71 and 0.73), whereas P7/8 showed significant inverse correlation with must sugar and pH (rs −0.83 and −0.85), as well as wine anthocyanins and glycerine (rs −0.79 and −0.73). In 2014, only P7/8 showed significant correlation with wine dry extract (rs 0.77).

Discriminant analysis on vintage effect on wine distinguished the vintages for all oenological variables, except alcohol and glycerine content (results not reported). The same outcome was obtained by the Fisher's LSD test (Table 4).

Principal component analysis (PCA), carried out on the wine features (alcohol, total acidity, polyphenols, anthocyanins, dry extract, glycerine, and colour intensity), showed clusters associated with MT (Fig. 5) more evidently than those associated with vintages. SAND and MAR wines, especially, showed strong differentiation from CALC and FLUV for Factor 1 (more related to polyphenols, anthocyanins, alcohol, dry extract and glycerine), whereas SAND and MAR were better differentiated between them by Factor 2 (related to colour intensity and total acidity).

The best differentiation among the wines occurred in vintage 2012, the driest and warmest, whereas in the other years only CALC wines were well discriminated (Fig. 5).

Analysing the three vintages pooled together, the discriminant

Table 4
Results of Fisher's LSD tests after one-way analysis of variance, using as grouping factor vintage, MT and UTB, respectively. Letters showed the groups significantly different for $p < 0.05$.

	Must			Final wine						
				after 6 months ageing						
	Sugar	pH	Malic acid	Alcohol	Tot. acid.	Polyphen.	Anthocyan.	Dry extr.	Glycer.	Colour int.
	$g \cdot L^{-1}$		$g \cdot L^{-1}$	%vol	$g \cdot L^{-1}$	$mg \cdot L^{-1}$	$mg \cdot L^{-1}$	$g \cdot L^{-1}$	$g \cdot L^{-1}$	
Vintage										
2012	220	3.27 (b)	0.7 (c)	13.2	6.0 (b)	1548 (c)	191 (b)	27.2 (b)	6.3	8.4
2013	225	3.28 (b)	1.5 (b)	13.5	6.6 (a)	2040 (a)	245 (a)	28.7 (a)	6.6	8.1
2014	223	3.19 (a)	2.3 (a)	13.4	6.8 (a)	1695 (b)	222 (a)	26.8 (b)	6.6	8.3
MT										
CALC	226 (a)	3.25 (b)	1.2 (c)	13.6 (a)	6.8 (a)	1760 (b)	245 (a)	28.2 (a)	6.5 (a)	9.7 (a)
SAND	223 (ab)	3.34 (c)	2.0 (a)	13.4 (ab)	5.7 (b)	1684 (b)	209 (b)	27.5 (ab)	6.6 (a)	6.6 (c)
MAR	216 (b)	3.14 (b)	1.2 (c)	12.9 (b)	6.8 (a)	1653 (b)	203 (b)	26.8 (b)	5.9 (b)	8.0 (b)
FLUV	225 (ab)	3.25 (b)	1.6 (b)	13.5 (ab)	6.7 (a)	1948 (a)	221 (ab)	28.0 (a)	6.9 (a)	8.8 (ab)
UTB										
CALC1	223 (ab)	3.25 (abc)	1.36 (cd)	13.4 (ab)	6.6 (ab)	1674 (bc)	243 (a)	28.1 (ab)	6.6 (abc)	9.4 (ab)
CALC2	230 (a)	3.26 (abc)	1.05 (d)	13.8 (a)	6.9 (a)	1846 (ab)	247 (a)	28.2 (a)	6.5 (abc)	9.9 (a)
SAND1	221 (ab)	3.31 (bc)	1.91 (ab)	13.3 (ab)	6.0 (bc)	1623 (c)	200 (b)	27.3 (ab)	6.6 (ab)	6.2 (d)
SAND2	226 (a)	3.38 (c)	2.13 (a)	13.6 (a)	5.5 (c)	1745 (bc)	217 (ab)	27.7 (ab)	6.5 (abc)	6.9 (cd)
MAR1	211 (b)	3.13 (c)	1.24 (cd)	12.7 (b)	6.8 (a)	1676 (bc)	209 (ab)	26.5 (b)	5.8 (c)	8.6 (abc)
MAR2	220 (ab)	3.16 (c)	1.24 (cd)	13.2 (ab)	6.7 (ab)	1639 (bc)	196 (b)	27.1 (ab)	6.1 (bc)	7.5 (bcd)
FLUV1	227 (a)	3.28 (ab)	1.57 (bc)	13.6 (a)	6.3 (ab)	1957 (a)	222 (ab)	27.8 (ab)	7.1 (a)	9.5 (a)
FLUV2	223 (ab)	3.22 (bc)	1.54 (bc)	13.4 (ab)	7.0 (a)	1939 (a)	220 (ab)	28.1 (a)	6.7 (ab)	8.0 (abcd)

analysis demonstrated that wines produced in the four MT were significantly different ($p < 0.05$) for colour intensity, glycerine and total acidity. Squared Mahalanobis distances showed the highest differences between CALC and SAND (13.3, $p < 0.01$) and between MAR and SAND (11.3, $p < 0.01$), whereas there were not significant differences between CALC and MAR, and CALC and FLUV.

Fisher's LSD test (Table 4) showed significantly lower wine total acidity and colour intensity in the wines from grapes produced on sandstone (SAND), and lower dry extract and glycerine content in the wines made from grapes on marine deposits (MAR). The latter also showed lower wine colour intensity as compared to wines from calcareous flysch (CALC) and ancient fluvial terraces (FLUV). The wines made from grapes produced on the ancient fluvial terraces had significantly higher polyphenols content, whereas grapes produced in the calcareous flysch provided significant higher anthocyanins and colour intensity.

When considering UTB as grouping variable instead of MT, the discrimination between groups in general did not increase. Fisher's LSD test showed several significant differences among the wines of the different UTB. On average, during the three experimental vintages, CALC2 wines provided the highest alcohol and colour intensity, SAND1 wines the lowest colour index, SAND2 the lowest total acidity, MAR1

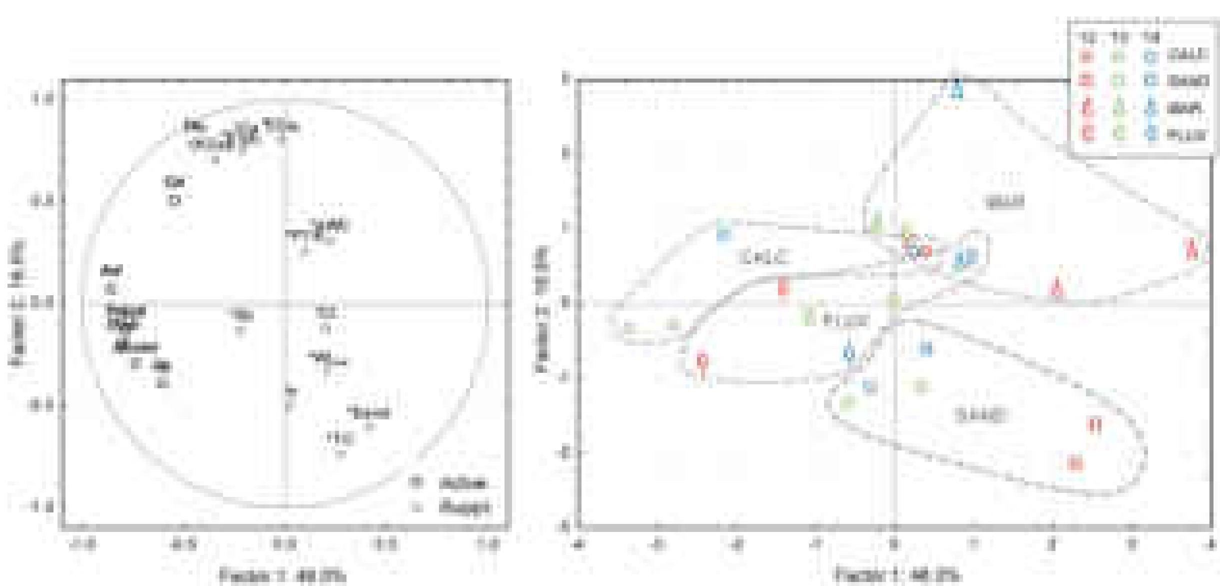

Fig. 5. PCA results. On the left, factor loadings of the active and supplemental (Suppl.) variables of PCA. On the right, factor scores of the PCA. The dashed polygons separate the four MT. The supplemental variables are pedological and climatic features not included in the calculation of PCA, but plotted in the graphs, according to the correlation with the PCA factors. Active variables: Alcohol, TAc-total acidity, Pol-polyphenols, Ant-anthocyanins, DExtr-dry extract, Gly-glycerine, Col-colour intensity/Supplemental: TC: gamma-ray total count, ECa_1 and ECa_2: apparent electrical conductivity 0–75 cm and 0–150 cm, Sk-stoniness, AWC: Available water capacity, Ca: total calcium carbonate, Clay, Sand, h: elevation, WI_{mod}: Winkler index modified (1 April–30 September), CI: Cool night index, P7/8: total precipitation in July and August. On the right, factor scores of the PCA.

Table 5
Results of mixed-design analysis of variance of the main must and wine features, using MT as fixed factor, vintage as random factor, and UTB as nested design in MT. In bold, significant values ($p < 0.05$).

Variable		% variability due to:						F			
			MT	Vintage	MT × vintage	UTB (MT)	Error	MT	Vintage	MT × vintage	UTB (MT)
		Effect	Fixed	Random	Random	Fixed		Fixed	Random	Random	Fixed
		df	3	2	6	4	8	3	2	6	4
Must	Must sugar		24.2	4.6	31.5	14.9	24.9	1.5	0.4	1.7	1.2
	Must pH		48.4	15.9	19.1	6.2	10.5	**5.1**	2.5	2.4	1.2
	Must malic acid		17.8	75.8	3.7	1.5	1.1	**9.6**	**61.3**	**4.3**	2.7
Wine	Total acidity		40.5	25.1	15.8	9.1	9.5	**5.1**	4.8	2.2	1.9
	Polyphenols		20.0	64.8	4.7	4.5	5.9	**8.4**	**41.0**	1.1	1.5
	Anthocyanins		23.4	45.4	20.7	2.6	7.9	2.3	**6.6**	3.5	0.7
	Dry extract		19.0	44.8	25.7	3.0	7.5	1.5	**5.2**	**4.6**	0.8
	Glycerine		43.5	4.3	26.6	6.4	19.2	3.3	0.5	1.9	0.7
	Colour intensity		56.0	1.1	30.0	11.2	1.7	3.7	0.1	**23.4**	**13.1**

the lowest alcohol content, and FLUV2 wines the highest total acidity.

On the other hand, Student's *t*-test and Mann-Whitney's *U* test did not show significant differences between the couples of UTB within a MT, with the only exception of significant higher total acidity in FLUV2 ($6.9\ g{\cdot}l^{-1}$) than in FLUV1 ($6.3\ g{\cdot}l^{-1}$) during the three years.

The results of mixed-design analysis of variance (Table 5), using MT as fixed effect, vintage as random effect, and UTB nested in MT, showed that:

- The variability of must pH, wine total acidity, glycerin and colour intensity were better explained by MT than climate variability of the different vintages.
- The content of must malic acid, wine polyphenols, anthocyanins and dry extract were more influenced by the vintage, although MT variability played an important role for anthocyanins and dry extract.
- UTB nested in MT explained very low variance, comparable with the variance of the error, with the only exception of colour intensity.

The F-test demonstrated that the wine produced in the different MT were significantly different ($p < 0.05$) for must pH and malic acid, wine total acidity, and polyphenols. Vintage showed a strong significant effect for must malic acid and polyphenols, and lower but still significant effect on anthocyanins and dry extract. Differentiation of wine colour intensity was mainly due to the interaction between MT and vintage, though UTB within each MT also showed a significant influence.

3.4. Wine sensory analysis

The blind sensory analysis of the wines produced in the 8 UTB provided results with very high standard deviation. This is also observable in the results of mixed-design analysis of variance of wine tasting parameters, where most of the variance percentage is explained by the error (Table 6).

This outcome can be due to the general high quality of the studied wine, however, the standardization and reliability of wine sensory analysis are very complicated issues and still subject to discussion (Rodríguez Donate et al., 2017; Cicchetti, 2017). Nevertheless, some remarkable wine peculiarities due to the terroir effect were recognizable and stable throughout the three vintages. The interaction between MT and vintage showed significant ($p < 0.05$) differentiation among wines for colour, flavour intensity, floral aroma, body and general evaluation. The effect of UTB enhanced the discrimination of the wines for colour, flavour intensity and fruity notes. On the other hand, herbaceous and spicy notes showed higher relationship with the vintage than with the MT or UTB.

The results of the wine tasting are summarized in Table 6. This table reports the results of the Fisher's LSD test after one-way ANOVA for each vintage, using UTB as the grouping factor and tasters as replicates. The results show that the differentiation of the wines, especially the differentiation between the couples of UTB within a same MT, decreased from 2012, the driest and warmest vintage, to 2014, the wettest and coldest year. The only exceptions were FLUV1 and 2, that tended to increase the differentiation in 2013 and 2014 for colour intensity in 2013 and for fruity notes in 2014 (Fig. 6).

SAND2 and SAND1 generally obtained the highest score among all wines, in all the vintages, for flavour and fruity notes, but SAND2 constantly outperformed SAND1 (Fig. 6). In 2012, also MAR1 and 2 were very different in terms of flavour, acidity and general score, whereas they became similar in 2013 and, in 2014. On the other hand, CALC1 and CALC2 never showed any significant differences in tasting.

4. Discussion

The results of this work demonstrated that, although climate of the vintage was extremely important for determining wine peculiarities, the role of terroir, at both scales (MT and UTB) was fundamental and stable over the years for several wine peculiarities.

According to the analysis of variance for must and wine features (Table 5), the effect of MT was stronger than that of vintage climate for must pH, wine acidity, glycerine and colour intensity. Macro-terroir played a strong role also in the aroma of the wine, as demonstrated by the wine tasting analysis (Table 7).

The climate conditions of the vintage were particularly important for must malic acid, polyphenols, anthocyanins and dry extract. On the other hand, the interaction between vintage and MT significantly affected the same wine variables (Table 4). Spatial variability of mesoclimate within a single vintage did not seem to effect the wine, since only few significant correlations between climatic indices (WI_{mod}, CI, and P7/8) and wine features were observed in 2013 (anthocyanins and glycerine) and in 2014 (dry extract).

The subdivision of two different UTB within a same MT, mainly based on homogeneous soil physical and hydrological features, seemed to play an important role only during dry summers, like in 2012 and, to a lesser extent, in 2013. The geometrical simplification of the cluster areas in UTB, needed to facilitate the grape harvest and to satisfy the minimal amount of grape for winery fermentation tanks, did not significantly decrease the variance between the groups of the variables used for clustering, with the only exception of CALC1 and 2 (Table 1). The CALC vineyards exhibited short-range soil spatial variability, mainly due to the stoniness percentage. For this reason, it was not possible to simplify the areas of the CALC clusters without loss of between-groups variability. In this case, the separated grape-harvest

Table 6
Results of mixed-design analysis of variance of the wine tasting indices, using MT as fixed factor, vintage as random factor, and UTB as nested design in MT. In bold, significant values ($p < 0.05$).

Tasting parameter	% variability due to:						F			
		MT	Vintage	MT × vintage	UTB (MT)	Error	MT	Vintage	MT × vintage	UTB (MT)
	Effect	Fixed	Random	Random	Fixed		Fixed	Random	Random	Fixed
	df	3	2	6	4	232	3	2	6	4
Colour		15.0	4.1	8.7	4.6	67.5	3.4	1.4	**5.0**	**4.0**
Flavour		0.2	4.3	5.3	4.8	85.3	0.1	2.4	**2.4**	**3.3**
Fruity		2.5	1.5	3.6	5.2	87.2	1.4	1.3	1.6	**3.5**
Floral		0.3	1.1	5.8	2.0	90.8	0.1	0.6	**2.5**	1.3
Herbaceous		0.1	8.0	1.2	3.3	87.5	0.2	**20.3**	0.5	2.2
Spicy		0.6	5.9	1.2	1.2	91.2	0.9	**14.7**	0.5	0.7
Body		1.6	3.8	11.6	0.8	82.2	0.3	1.0	**5.5**	0.6
Acidity		4.3	4.9	4.4	1.2	85.3	1.9	3.3	2.0	0.8
General eval.		0.6	0.5	17.6	1.8	79.4	0.1	0.1	**8.6**	1.3

should be done in small and scattered areas to highlight the UTB effect on wine (Bramley et al., 2011a, 2011b). This could be possible only through selective harvest managed by GPS and digital maps.

From the oenological and wine tasting results, the wine produced in the different MT and UTB showed the following features:

- Clayey-calcareous soils developed on Cretaceous calcareous flysch (CALC), one of the most representative MT of Chianti Classico wine district (Fig. 1), provided wines with general higher alcohol, total anthocyanins, dry extract and colour intensity than average. A similar study (Priori et al., 2013a, 2013b) was carried out in other vineyards of the farm on clayey-calcareous flysch, during the vintage 2010. The wines showed similar high colour intensity (from 9.1 to 11.6), alcohol (13.6–14.2%vol) and polyphenols (1823–2004 $mg \cdot L^{-1}$). In a previous study, also Scalabrelli et al. (2001) reported higher anthocyanins, total acidity and dry extract than the average on wines produced from grapes cultivated on calcareous flysch. Wine tasting confirmed that such wines have generally higher colour intensity and general high fruity flavour and medium-high acidity and body. These characteristics corroborate the review of Italian terroir and wine features of Ricci Alunni (2004), who reported high alcohol and colour intensity as main features of the wines produced on calcareous-clayey soils. The differences between the wines produced in CALC1 and CALC2 were not significant. Indeed, the geometrical simplification of CALC UTB areas caused the loss of the very detailed soil spatial variability within the vineyard.
- Loamy-sand soils, developed on feldspathic sandstone (SAND), which are very common at the higher altitude of the Chianti hills, characterized the wine with light colour intensity and low acidity. The grapes in our trial had higher must pH and malic acid, whereas the total acidity of wines was around −15% of the average, and lower colour intensity. Ricci Alunni (2004) described the wines produced on sandy non calcareous soils as elegant, scented, but scarce in colour. The inverse relationship between soil pH and wine pH has been also found by other authors (Retallack and Burns, 2016). Lower acidity of the wines produced in SAND terroir, could be due to two main causes: high content of potassium and very low content of calcium carbonate in the soil. Several authors (Morris et al., 1983; Mpelasoka et al., 2003) reported that high potassium content in soil, due to natural causes or to fertilization, tends to increase must and wine pH. The same authors reported a negative effect of high potassium on wine colour, which is lighter. High concentration of potassium in grape juice tends to decrease the concentration of free acids, such as tartaric acid (Kodur, 2011). During wine fermentation, potassium tends to bind with tartaric acid, with a consequent precipitation of potassium bitartrate (Kodur, 2011). This process causes tartaric acid of the wine to decrease, and hence the increase of wine pH. The direct relationship between content of potassium in soil and in grape must has been reported in many other studies (e.g., Freeman and Kliewer, 1983; Chan and Fahey, 2011), however it was not tested for this study.

The wine tasting showed higher flavour intensity and fruity and floral notes in SAND2 than in SAND1 in all the vintages. The causes of the positive effect of the SAND2 soil features on wine flavour should be analysed in more detail to understand which parameters are involved. Similar to the findings of González-Barreiro et al. (2015), it is likely that higher drainage and soil porosity of SAND2, as well as lower grapevine vigour contributed to the grape aroma precursors. These UTB were mainly differentiated by the slope and for the ECa_1, which was significantly lower in SAND2 and indicated a significant higher soil

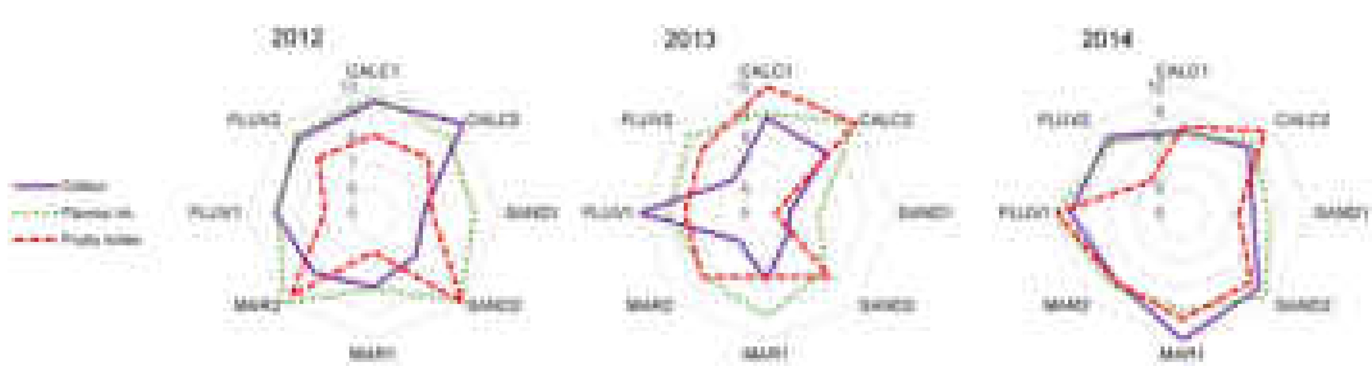

Fig. 6. Spider graphs reporting the means of the most significant wine tasting parameters (colour, flavour intensity, and fruity notes) for each UTB in the three vintages. The axis scale was standardized 0 to 10 for all the parameters, setting the maximum value of each parameter for that vintage to 10.

Table 7
Results of Fisher's LSD tests after one-way ANOVA for each vintage, using UTB as grouping factor and tasters as replicates. Letters showed the groups significantly different for $p < 0.05$. In bold, significant differences ($p < 0.05$) between the UTB couples of each MT.

Vintage	UTB	Flavour						Taste		Gen. score
		Colour	Intensity	Fruity	Floral	Vegetal	Spicy	Body	Acidity	
2012	CALC1	9.0 (ab)	8.7 (ab)	2.1 (abc)	2.1 (ab)	1.5 (a)	1.9 (a)	8.5 (a)	8.0 (abc)	8.3 (abc)
	CALC2	9.6 (a)	8.3 (ab)	2.1 (abc)	1.9 (ab)	1.3 (a)	1.5 (a)	8.4 (a)	6.9 (cd)	7.2 (cd)
	SAND1	6.7 (e)	8.1 (ab)	**1.9 (bc)**	2.0 (ab)	1.5 (a)	1.6 (a)	7.9 (a)	**7.2 (bc)**	8.6 (ab)
	SAND2	7.1 (de)	8.9 (a)	**2.6 (a)**	2.4 (a)	1.5 (a)	1.9 (a)	8.3 (a)	**6.0 (d)**	8.2 (abc)
	MAR1	7.6 (cde)	**7.2 (b)**	**1.7 (c)**	1.8 (b)	1.8 (a)	1.6 (a)	7.3 (a)	**7.8 (bc)**	**6.7 (d)**
	MAR2	8.0 (cd)	**9.0 (a)**	**2.5 (ab)**	2.2 (ab)	1.2 (a)	1.6 (a)	8.6 (a)	**8.7 (a)**	**8.9 (a)**
	FLUV1	8.5 (bc)	7.9 (ab)	1.8 (c)	2.2 (ab)	1.9 (a)	1.6 (a)	7.2 (a)	8.5 (ab)	7.9 (abcd)
	FLUV2	8.8 (ab)	8.4 (ab)	2.1 (abc)	2.1 (ab)	1.5 (a)	1.8 (a)	7.2 (a)	8.4 (abc)	7.5 (bcd)
2013	CALC1	8.6 (ab)	7.7 (ab)	2.8 (a)	2.7 (a)	1.7 (a)	1.9 (ab)	8.5 (ab)	7.3 (a)	8.6 (ab)
	CALC2	8.2 (ab)	8.6 (a)	2.8 (a)	2.5 (ab)	1.7 (a)	2.5 (ab)	9.1 (a)	7.0 (a)	9.7 (a)
	SAND1	5.8 (d)	**6.1 (c)**	**1.5 (b)**	**1.5 (c)**	2.1 (a)	1.8 (ab)	6.3 (d)	7.4 (a)	5.5 (d)
	SAND2	6.1 (d)	**7.1 (ab)**	**2.4 (a)**	**2.2 (ab)**	1.7 (a)	2.2 (ab)	6.8 (cd)	6.9 (a)	6.6 (cd)
	MAR1	**7.5 (b)**	7.8 (ab)	2.1 (a)	1.9 (bc)	2.3 (a)	2.2 (ab)	**7.9 (abc)**	7.6 (a)	8.2 (b)
	MAR2	**6.4 (cd)**	7.3 (ab)	2.4 (a)	2.5 (ab)	1.4 (a)	2.6 (a)	**6.6 (d)**	7.5 (a)	7.8 (bc)
	FLUV1	**9.8 (a)**	7.6 (ab)	2.3 (a)	1.9 (bc)	1.6 (a)	2.4 (ab)	**7.7 (b)**	8.0 (a)	**8.2 (ab)**
	FLUV2	**6.7 (cd)**	8.0 (a)	2.4 (a)	2.5 (ab)	1.9 (a)	1.8 (b)	**6.6 (cd)**	8.0 (a)	**6.5 (cd)**
2014	CALC1	7.4 (bc)	7.6 (b)	2.1 (abc)	1.8 (ab)	1.4 (a)	2.0 (a)	7.6 (ab)	8.2 (ab)	7.0 (b)
	CALC2	7.8 (abc)	8.3 (ab)	2.4 (a)	2.0 (ab)	1.2 (a)	1.6 (a)	7.3 (b)	8.6 (ab)	7.2 (b)
	SAND1	**7.0 (c)**	**7.8 (b)**	1.8 (bc)	2.2 (ab)	1.4 (a)	1.4 (a)	8.4 (a)	8.4 (ab)	8.1 (ab)
	SAND2	**8.3 (ab)**	**9.0 (a)**	2.2 (abc)	2.4 (ab)	1.0 (a)	1.7 (a)	8.5 (a)	7.7 (b)	8.8 (a)
	MAR1	**9.0 (a)**	8.2 (ab)	2.3 (ab)	2.2 (ab)	1.0 (a)	1.7 (a)	8.5 (a)	8.8 (a)	8.0 (ab)
	MAR2	**7.9 (bc)**	8.4 (ab)	2.2 (abc)	1.9 (ab)	0.7 (a)	1.5 (a)	7.9 (ab)	8.1 (ab)	7.7 (ab)
	FLUV1	8.5 (ab)	**9.3 (a)**	**2.5 (a)**	1.6 (b)	0.9 (a)	1.3 (a)	8.8 (a)	8.2 (ab)	8.0 (ab)
	FLUV2	8.3 (abc)	**8.3 (b)**	**1.7 (c)**	2.0 (ab)	1.1 (a)	1.4 (a)	8.7 (a)	8.6 (ab)	8.3 (ab)

stoniness.

- Loamy and loamy-sandy soils developed on marine sands (MAR), common in a wide area of the southern-central Tuscany, such as the "Nobile di Montepulciano DOCG" (Priori et al., 2014b, and Costantini et al., 2012) and "Chianti DOCG" districts (Pollini et al., 2014), provide wines with low (MAR1) or medium (MAR2) alcohol, as well as low glycerine and dry extract. Very similar values of must sugar content and total polyphenols were reported in Sangiovese wines in the southern area of Chianti DOCG by Costantini et al. (2009 and 2010). Scalabrelli et al. (2001) reported that wines made by Sangiovese cv. grapes, cultivated on marine sandy deposits in Chianti Classico DOCG area, were characterized by lower anthocyanins and dry extract, as well as higher total acidity, than the average Chianti wines. Water availability seems to play a key role in this MT since MAR needs a moderate water deficit to produce wines recognizable by high fruity-floral aroma. The two UTB of this MT showed significant differences of ECa_1, ECa_2 and gamma-ray TC, which showed higher values in MAR1. MAR2, characterized by sandy-loamy soils, very low fertility, rich in gravel, and with high internal drainage, produced wines characterized by general high flavour intensity and higher fruity and floral notes than MAR1. The differences between the two UTB disappeared during vintage 2014, the most humid year, therefore, a separated grape-harvest is useless in these conditions.
- Loamy and clay-loamy soils, calcareous, developed on fluvial terraces (FLUV), made wine richer in alcohol, polyphenols, and glycerine, as well as high colour intensity. FLUV1 showed significantly higher ECa_1 and ECa_2, mainly due to lower sand content and stoniness than FLUV2. According to wine tasting, the wines of FLUV1 had higher colour intensity in 2013 and in 2014 higher fruity notes than FLUV2. Very few studies reported the *Sangiovese cv.* wine features in this type of MT because it is not widespread in this area. The studies of Bucelli et al. (2010) and Priori et al. (2014b), that addressed viticultural zoning in the province of Siena, reported some results of *Sangiovese cv.* cultivated on calcareous soils of fluvial terraces in Brunello di Montalcino DOCG, approximately 50 km west-southward. This province-scale study demonstrated that this type of terroir provides wines generally higher in alcohol and polyphenols than the average of the province.

5. Conclusions

The four MT studied in this work, which represent soil and lithological features typical of many vineyards of the Chianti Classico wine district, produced wines with different peculiarities through vintages with contrasting climate. The parameters that better showed MT effect were must pH, wine total acidity, glycerine and colour intensity. Climate of the vintage instead played a major role on the content of must malic acid, polyphenols, anthocyanins, and dry extract.

In general, the vineyards on clay-calcareous flysch (CALC) produced wines with the highest colour intensity, alcohol, anthocyanins and dry extract, whereas those on feldspathic sandstone (SAND) produced wines with the weakest colour and the lowest total acidity.

The marine deposits (MAR) wines showed lower dry extract and glycerine than the average, and intermediate colour intensity, whereas the ancient fluvial terraces (FLUV) wines showed higher polyphenols, dry extract, and glycerine content. Wine tasting confirmed the results of analytical data in that CALC provided wines with the strongest colour, whereas SAND wines with the lowest colour and acidity.

Differences between the UTB within a same MT were not stable over the three contrasting vintages. The rainiest summer of 2014 showed the weakest tasting differences of the wines produced in the two UTB of a same MT. This was mainly due to the primary features discriminating two UTB within a same MT, which were stoniness, soil depth, water holding capacity, and water permeability (K_{sat}). These soil variables are strictly related to plant water nutrition, so they have a major influence on grape quality in dry summer. On the contrary, wet summers like 2014 smooth the differences in wine peculiarities between UTB in a same MT, making the costs of a separated grape-harvest unnecessary.

In conclusion, geology, soilscape and climate features, which characterize MT, drive some major wine peculiarities over time, while soil physical-hydrological features, which typify UTB within the same MT, play a key role on wine distinctiveness, mainly during dry vintages. The use of a more robust delineation of homogeneous areas, performed using soil maps obtained by proximal sensors, is fundamental to discriminate UTB within vineyard. On the other hand, selective harvest of small and scattered UTB within a vineyard is possible only if digital maps and GPS are used, both for the manual and the mechanical harvest.

The outcomes of this study are of particular interest since it was this variability of natural conditions under which the original “formula” of the Chianti wine was conceived.

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