

AN ABSTRACT OF THE THESIS OF

Xiaoxi Yuan for the degree of Master of Science in Food Science and Technology presented on June 6, 2017.

Title: Effect of Regulated Deficit Irrigation on Malbec and Syrah Grape and Wine Quality

Abstract approved:

Michael C. Qian

The water status of grape vine throughout the growing season is a primary determinant of vine vigor and berry composition. The concentrations of volatile compounds and precursors in grape berries are highly influenced by viticultural practices. Imposing a water deficit on the vine during berry development is an important vineyard management strategy to alter grape and wine quality. Although much literature has reported the impact of vine water status on grape composition and volatile compounds, the results are still inconclusive due to the variations in irrigation regimes, cultivars and other agronomical conditions. The detailed chemical compound responsible for the flavor attribute differences need to be fully studied. Accordingly, this study was conducted to evaluate the impacts of regulated deficit irrigation (RDI) on the volatile composition of Malbec and Syrah grapes and wines.

Malbec and Syrah grape chemical and volatile composition was investigated over three consecutive growing seasons (2014-2017) in established field trials located at the University of Idaho Parma Research and Extension Center in Parma, ID (lat: 43°78'N; long: 116°94'W; 750 m asl). Four irrigation regime (70 % ETc from fruit set to veraison, 35 % ETc from veraison to harvest (70/35), 70% ETc sustained from

fruit set to harvest (70/70), 35 % ETc from fruit set to veraison, 70 % ETc from veraison to harvest (35/70), and 35% ETc sustained from fruit set to harvest (35/35)) was applied to the vines with two irrigation frequencies (1x= one event per week, 3x=same irrigation amount apportioned into three irrigation events per week). Berry volatile compositions were analyzed by Solid Phase Micro Extraction-Gas Chromatography-Mass Spectrometry (SPME-GC-MS). Results showed that different irrigation frequency barely affected the volatiles in Malbec grapes but have greater influence on volatile composition of Syrah grape. ETc variation before veraison and after veraison influenced C₁₃-norisoprenoids precursor content in Malbec and Syrah berries. 70% ETc before veraison contributed to higher bound-form trans- β -damascenone concentration in Malbec berries, while both 35% ETc before and after veraison resulted in a higher bound-form TDN and vitispirane concentration in Syrah berries. In this study, the YAN (yeast assimilable nitrogen) showed a correlation with irrigation amount in 2015's and 2016's Syrah grapes and 2016's Malbec grape berries. The 70/70 irrigation amount resulted in a relatively lower YAN concentration in grape must of 2016's Malbec and 2015 and 2016's Syrah.

Wines were made with experimental grape samples, and wine compositions were analyzed using GC-FID, GC-PFPD and GC-MS. Results showed that wine volatile compositions of both Malbec and Syrah were affected by irrigation amounts, but barely affected by irrigation frequency. The terpenoid concentrations in wine were more related with the bound-form terpenes in grapes rather than free form terpenes. Irrigation frequency and amount showed no influences on either free form or bound form C₁₃-norisoprenoids in Syrah wines, but bound form TDN and vitispirane concentrations in Malbec wines were affected by irrigation amount. The esters, higher alcohols and fatty acids content in wines were closely related with the YAN levels in grape must before fermentation. The lower YAN concentration led to a higher ethyl acetate and lower Phenylethyl alcohol, isobutyl alcohol and isoamyl alcohol concentrations in corresponding wines. The YAN level in grape juice was affected by water status of the grape vine, while the YAN level can be associated with aroma-active compounds in wine. Thus, imposing water deficit to the grape vine can alter the volatile composition of the final wine.

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Effect of Regulated Deficit Irrigation on Malbec and Syrah Grape and Wine Quality

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APPROVED:

Major Professor, representing Food Science and Technology

Head of the Department of Food Science and Technology

Dean of the Graduate School

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CONTRIBUTION OF AUTHORS

Dr. Michael Qian contributed to the overall research concept, research design, data interpretation and revision. Dr. Yanping Qian provided supervision and assistance for volatile analysis of this work. Dr. Krista Shellie contributed to the field experimental design, sample collection, assisted the interpretation of the data, and did manuscript revision in Chapter 2. Dr. James Osborne contributed to the winemaking in Chapter 3.

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CHAPTER 1 LITERATURE REVIEW

Wine is an ancient alcoholic beverage with distinguishable and unique flavors made from grape berries. The sensation of wine flavor occurs when odor-active molecules released from wine stimulate human sensors, which the human brain interpret as overall flavor perception (Taylor 1998). Since the final sensorial flavor of wine depends on both taste and aroma, the composition of aroma compounds in wine can influence the wine aroma and overall wine flavor.

Given that wine quality is primarily associated with the entire viticulture and winemaking process, understanding the relationships among viticulture practices, winemaking process and wine quality is the main focus for many grape growers and winemakers (Jackson 2008). The flavors of wine, including the tastes and aroma of wine, originate from the grapes, wine fermentation process and maturation process. Considered to be one of the most important characteristics of wine, wine aroma has been studied in the past few decades. The composition of volatiles contributes to the distinguishing wine aroma of different varieties.

1.1 The origin of wine aroma

The aroma of wine is complex. More than 800 compounds have been reported in the literature that contribute to the wine aroma with a concentration range from ng/L to mg/L, which covers different classes of aroma compounds including thiols, amines, esters, lactones and alcohols. The chemical profile of wine is derived from multiple origins, including a direct contribution of grape-derived aroma compounds, fermentation-derived compounds and aroma compounds generated during aging and storage (Anderson et al. 1975, Dunlevy et al. 2009, González-Barreiro et al. 2015). Some wine volatile compounds are linked with grape components, such as monoterpenes and

methoxypyrazines, which have little alternation during fermentation process. Most of the odor-active compounds are produced during fermentation, such as higher alcohols, esters, aldehydes, terpenes, phenols and sulfur compounds (Hernández-Orte et al. 2006).

1.1.1 Grape-derived aroma compounds

Although most of the odor-active compounds are generated through fermentation, grape-derived aroma compounds are significant to the sensory attributes of wine. Aldehydes, ketones, alcohols, esters and furans are the major compounds that contribute to grape aroma. These compounds exist in grape in both free form and bound form. Free volatile compounds are released through endogenous enzymes during berry crushing. On the contrary, bound volatile compounds do not directly contribute to the grape aroma but can be released during fermentation, maturation and storage. Grape-derived volatile compounds are secondary metabolites, which can be altered by environmental conditions, vineyard management, harvest time, and can be influenced by genes expression in the biosynthesis pathway (Dunlevy et al. 2009). By understanding the biosynthesis pathways and the sensory characteristics of grape-derived volatile compounds can help wine makers to improve the wine-grape and wine quality from the vineyard. The biosynthesis pathway and the sensory characteristics of major groups of flavor compounds will be reviewed in the following section.

Aliphatic volatile compounds

Aliphatic volatile compounds originate from fatty acid oxidation and amino acid degradation. The dominant grape-derived aliphatic volatile compounds are short straight chain or branched-chain aldehydes and alcohols (Dunlevy et al. 2009). The major aliphatic volatile compounds in grapes include C₆-aldehydes and C₆-alcohols, derived from the lipoxygenase pathway (Salas et al. 2000). Figure 1.1 shows the biosynthesis pathway of aliphatic volatile compounds. The C₆ compounds are characterized by their grassy and leafy aroma. The most important C₆ compounds in grapes include hexanol, cis-2-hexenol, cis-3-hexenol, trans-2-hexenol, trans-3-hexenol, hexanal, and trans-2-

hexenal. In addition to C₆ compounds, C₉ straight chain volatile compounds and methyl branched chain volatile compounds are other minor constitution of the grape volatile profile. In most cases, the aliphatic aroma compounds in grapes have a distinguished green or leaf-like sensory descriptor (Table 1.1). During the wine making process, these aliphatic compounds in grapes are converted to alcohols and esters, usually with positive sensory attributes (Palomo et al. 2007). C₆-aldehydes are mainly responsible for the green aroma of grapes, but usually not present in wine, since most of them have been converted to the C₆-alcohols. The E-2-hexenal is rapidly reduced to n-hexenol via trans-2-hexenol during fermentation (Joslin and Ough 1978).

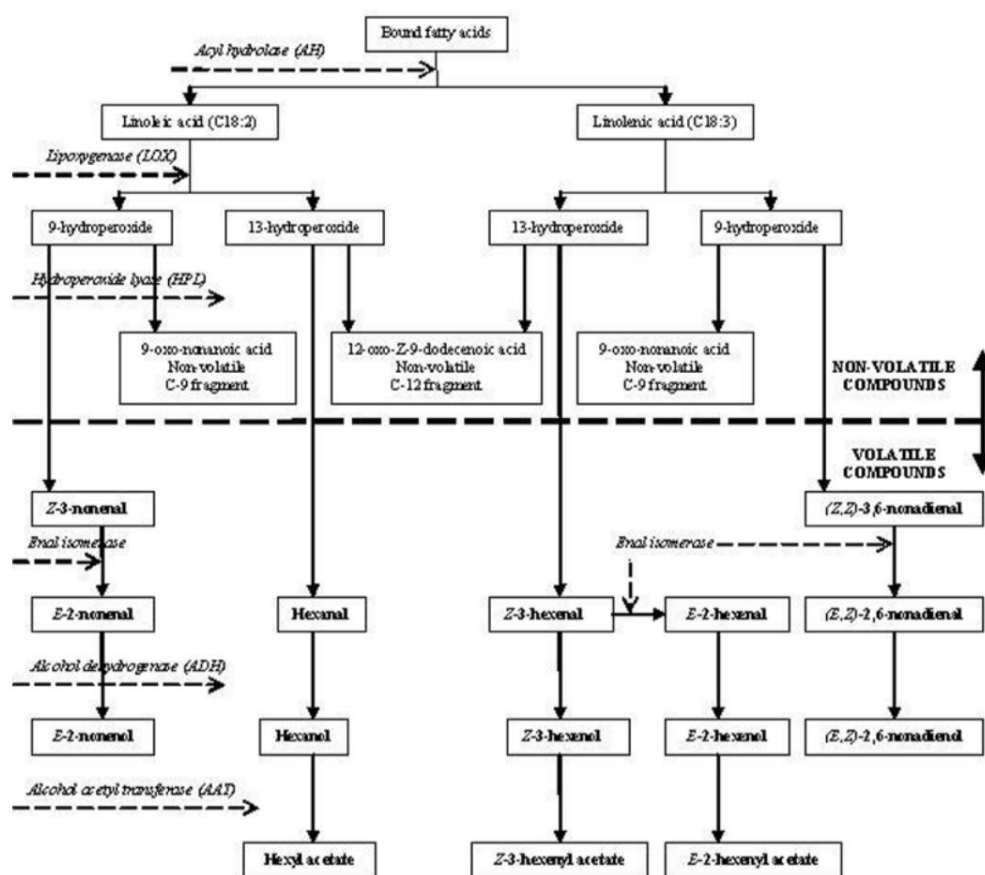


Figure 1.1 Biogenesis of lipid derived volatile compounds in grapes

Volatile compounds are shown in bold, dashed arrows present enzymes. Figure reference: Dunlevy et al. 2009

Table 1.1 Odors of common grape aliphatic volatile compounds

Compounds	Odor descriptor	Odor threshold (ug/L)
Hexanal	Grassy	4.5
(E)-2-Hexenal	Green, lemon	17
Hexanol	Resin, green	8000
(Z)-3-Hexenol	Green	400
(E)-2-Hexenol	Green	500
Hexyl Acetate	Banana, pear	2

Table reference: Buttery et al. 1971, Larsen and Poll 1992, Dunlevy et al. 2009

It is believed that C₆ compounds are indicators of grape maturity. Fang and Qian (Fang and Qian 2012) have reported that the concentration of C₆ compounds is related to the maturity and variety of grapes. The concentration of C₆-aldehydes shows an increasing trend after veraison until the grapes reach the harvest maturity and then decreases. The C₆-alcohols, however, continuously decreases during grape ripening.

There is little research about the effect of vineyard management practices on C₆ compounds. Research shows that water status influences the levels of C₆ compounds in grapes (Mendez-Costabel et al., 2014; Song et al., 2012). The C₆ compounds from vines with no rainfall were lower compared to the vines under normal rainfall conditions in Merlot (Mendez-Costabel, 2014). Song et al. (Song et al., 2012) reported that the concentration of free C₆ compounds in Merlot grapes decreased when deficit irrigation was applied. It is reported that the concentration of C₆ compounds in Merlot are season-related (Mendez-Costabel et al. 2013). However, the change of C₆ compounds in grapes is not observed in many studies, which might be due to the different grape variety and weather conditions (Kalua et al., 2010).

Terpenoids

Terpenoids make up the largest class of plant secondary metabolites (Dunlevy, Kalua et al. 2009), and are the most studied grape-derived volatile compounds in wines (Rapp and Mandery 1986). Terpenoids, which can be classified into 5 subgroups, hemiterpenes (C₅), monoterpenes (C₁₀), sesquiterpenes (C₁₅), homoterpenes (C₁₁ and C₁₆),

and diterpenes (C_{20}), based on the numbers of carbon, originate from the universal five-carbon precursor, dimethyl allyl diphosphate (DMAPP) and isopentenyl diphosphate (IPP) (Dudareva et al. 2006). Among these terpenoids, monoterpenes appear to be the most dominant terpenes influencing grape and wine aroma. In general, monoterpenes are formed by biosynthesis, the content of monoterpene fractions increase with maturation of the grape berries (Razungles et al. 1993). About 70 monoterpenes have been identified in grapes and wines (Rapp 1998), among which linalool, geraniol, nerol, citronellol and α -terpineol (Mateo and Jiménez 2000) are the prominent free monoterpene alcohols found in grapes and have the greatest sensory impacts on the wine (Figure 1.2) (Styger et al. 2011). Other important monoterpene compounds include monoterpene ethers, for example rose oxide and linalool oxide, and polyhydroxylated monoterpenes (Williams, Strauss et al. 1985).

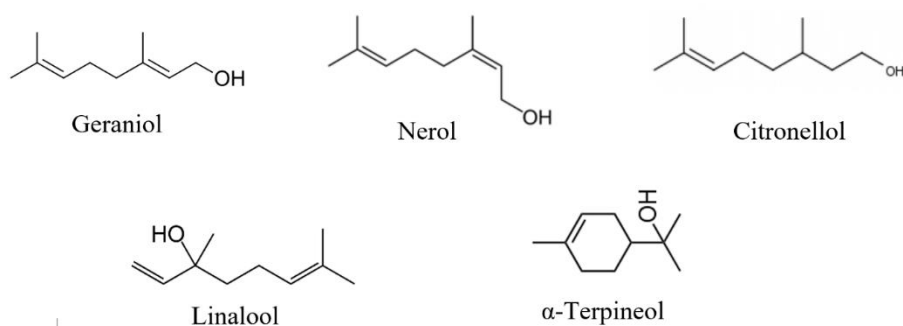


Figure 1.2 Common grape monoterpene alcohols

Studies have shown that terpenoids contribute floral and fruity aromas to the wines (Câmara et al., 2004). Monoterpenes are the major sources for the fruity and floral aromas in wine. Grape varieties can be classified based on the level of monoterpenes in grape berries (Strauss et al. 1986). Based on the concentration level of monoterpenes, Strauss et al. (Strauss et al. 1986) divided red and white wine grape cultivars into three groups: cultivars with high free monoterpenes level (up to 6mg/L) are Muscat varieties, grapes with concentration of 1-4 mg/L free monoterpenes are non-Muscat aroma varieties, and neutral varieties in which monoterpenes do not appear to influence flavor. In general, the high free monoterpene level in grape appears to show more Muscat-type character,

while moderate levels of free monoterpenes are usually associated with floral varieties. Monoterpenes are the key floral aroma compounds for the floral grape varieties, but monoterpenes in the non-floral varieties, such as Pinot noir, are usually below their threshold values (Chatonnet et al. 1992).

Monoterpenes are stored in berries as free volatiles and as sugar-bound precursors (Wilson et al. 1986). However, only a small portion of monoterpenes are present as free form volatiles, while the majorities are bounded to sugars as glycosides, or occur as non-volatile di- or tri-ols, that do not contribute to wine aroma (Maicas and Mateo 2005, Bakker and Clarke 2011). During fermentation, terpene glycosides can be hydrolyzed by acids (Williams et al. 1982) or enzymes (Gunata et al. 1985) to free form monoterpenes. Under acidic conditions, glycosides will lead to a molecular rearrangement of the monoterpenes, which will transform into other compounds (Mateo and Jiménez 2000). During winemaking and aging, both acid and enzyme hydrolysis may occur. During aging, some monoterpenes may increase due to the release of free terpenes from glycosides, such as α -terpineol. Decreases may result from the oxidation or other transformation, such as linalool to linalool oxide (Jackson 2008).

The concentration of terpenes in grapes were variety-dependent (Strauss et al. 1986). Climate also showed impacts on terpenes concentration in grape berries (Ji and Dami 2008). Vineyard management such as deficit irrigation and cluster zone leaf removal that associated with sunlight exposure, can influence the terpene concentration in grape (Ji and Dami 2008, Song et al. 2012).

C₁₃-norisoprenoids

Norisoprenoids are common plant volatiles contributing to the flower-like and fruity aroma. Norisoprenoids consisting of carbon atoms of 8, 9, 10, 11, 13, 15 and 18 have been reported as degradation of carotenoids (Wu et al. 1999, Lewinsohn et al. 2005). C₁₃-norisoprenoids, well-known for their extremely low sensory thresholds, are significant sources of grape-derived flavors in wines (Dunlevy et al., 2009). However, only a few

free norisoprenoids can be found in grape, while most norisoprenoids accumulated in wines existed as non-volatile and odorless precursors in grape berries until released by acid hydrolysis or enzymatic hydrolysis (Williams et al. 1992). Many C₁₃-norisoprenoids in grape berries have been identified, but only a few of them show significant influence on wine flavors, including β -damascenone, β -ionone, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), vitispirane, and (*E*)-1-(2,3,6-trimethylphenyl) buta-1,3-diene (TPB) (Dunlevy et al., 2009). Their chemical structures are showed in Figure 1.3.

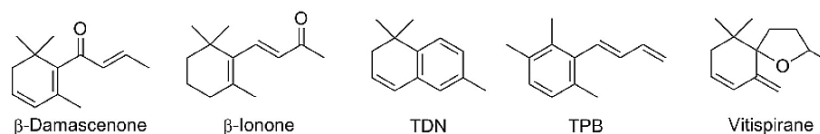


Figure 1.3 Chemical structures of some important C₁₃-norisoprenoids in grapes

β -damascenone, described as fruity, floral, and honey-like aroma, is a key volatile compound in grape and many other fruits with an extremely low sensory threshold at 2 ng/L in water, but with a very wide range of odor threshold in red wines depending on the wine matrix (Buttery et al. 1988, Pineau et al. 2007). Studies have reported that when β -damascenone is present below its threshold in wines, it will enhance red fruit aromas by interactions with other compounds (Pineau et al. 2007). β -ionone, often described as sweet or violet aroma, is another significant compound in wines and has a low sensory threshold at 7 ng/L in water (Buttery et al. 1990, Winterhalter and Rouseff 2002). The concentrations of β -damascenone and β -ionone in grapes and wines, are usually above their sensory thresholds (Fang and Qian 2005, Bindon et al. 2007, Ristic et al. 2010). Therefore, they are important aroma contributors to many wine varieties such as Merlot, Cabernet Sauvignon and Pinot noir (Fang and Qian 2005; Gürbüz et al. 2006; López et al. 1999). While β -damascenone and β -ionone have a positive influence on wine aroma, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) has a negative influence on grape and wine flavor for its kerosene-like aroma with a sensory threshold of 20 μ g/L in both model wine and natural white wines (Sacks et al. 2012). In grape berries and young Riesling wines, TDN usually has a concentration below its detection threshold without sensory

impact on the berries and wines. However, with aging, TDN levels can increase dramatically above its threshold, and has potentially negative sensory attributes on the wine (Simpson 1978). Vitispirane is an important odorant in bottle-aged Riesling wine (Simpson and Miller 1983) with a sensory threshold of 800 $\mu\text{g/L}$ (Simpson et al. 1977). Vitispirane has two pairs of diastereomers, which gives different aromas. The cis-vitispiranes are fresher with a green odor of chrysanthemum with an additional flowery-fruity wine note. The trans-vitispiranes have a heavy scent of exotic flowers with an earthy-woody note (Schulte-Elte et al. 1978). Although vitispirane has been detected in many wine varieties, similar to TDN, its concentration is commonly below its sensory threshold and shows no sensory impact (Eggers et al. 2006).

It is reported that the C_{13} -norisoprenoids arise from carotenoid precursors found in grapes. The major carotenoids (85% of the total) are β -carotene and lutein. Other carotenoids include neochrome, neoxanthin, violaxanthin, luteoxanthin etc. (Mendes-Pinto 2009). The carotenoids reported to be directly associated with wine aroma are β -carotene and neoxanthin, while lutein and violaxanthin can also be considered as aroma precursors since they may also produce norisoprenoid compounds (Winterhalter and Rouseff 2002). Because of the highly-conjugated double-bond structure, carotenoids are unstable and likely to be broken down by acids and enzymatic hydrolysis during fermentation yielding norisoprenoids. The generation of norisoprenoids in plants includes three steps: first, with dioxygenase, carotenoids undergo oxidative cleavage to produce primary cleavage products, then, enzymes transform the primary cleavage products to the intermediate metabolites, and finally, acid catalyzes conversion of these non-volatile intermediate metabolites into the volatile aroma compounds (Winterhalter and Rouseff 2002). The formation of β -damascenone from neoxanthin by both enzymatic and non-enzymatic pathway is illustrated in Fig 1.4. The generation of β -ionone from β -carotene can be caused by multi-pathways, including β -carotene cleavage by cleavage dioxygenases, photo-oxygenation and thermal degradation (Isoe et al. 1969, Kanasawud and Crouzet 1990).

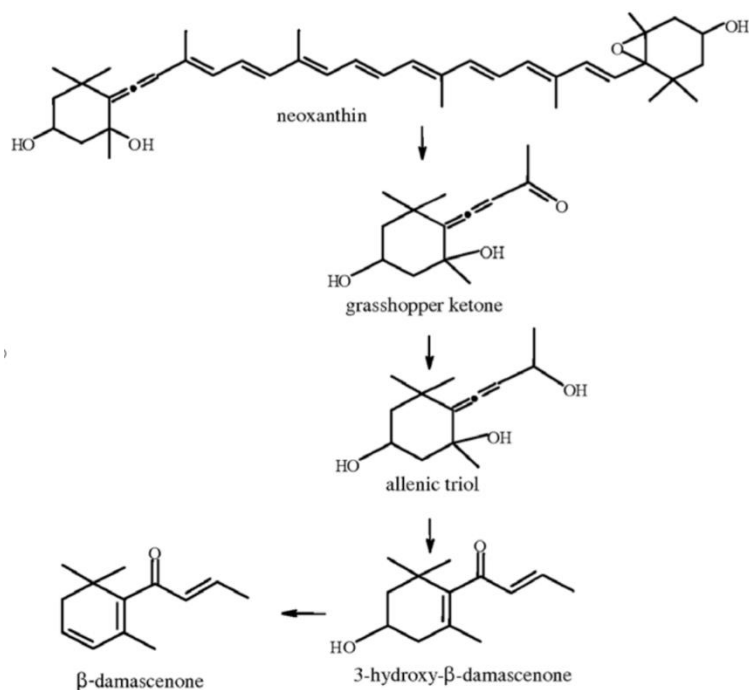


Figure 1.4 The formation of β -damascenone from neoxanthin
(Winterhalter and Rouseff 2002)

Carotenoid breakdown products in grapes during maturation includes C₁₃-norisoprenoids, which can be more or less relevant to the viticulture condition (Lee et al. 2007). The release of glycoside-bonded norisoprenoids by acid hydrolysis and enzyme hydrolysis during fermentation has been suggested to have major contribution to norisoprenoids in wine (Gunata et al. 1985, Strauss et al. 1987, Winterhalter and Rouseff 2002). In young wines, C₁₃-norisoprenoids arise directly from grape berries and those released during fermentation process. Wine storage and aging conditions will also affect the development of C₁₃-norisoprenoids, especially at high temperature and oxygen, which stimulate formation of C₁₃-norisoprenoids in wine (Winterhalter et al. 1990, Ferreira and de Pinho 2004). The overall contribution of C₁₃-norisoprenoids to the wine aroma is made by free C₁₃-norisoprenoids in grape berries, and the free form C₁₃-norisoprenoids after the acid or enzymatic hydrolysis their precursors during fermentation and the chemical reactions in wine aging and storage stage.

The concentration of C₁₃-norisoprenoids in grapes can be altered by viticultural practices including leaf removal (Feng et al. 2015), deficit irrigation (Song et al. 2012) and fertilization level. Climatic conditions have also been reported to influence the carotenoids, which might affect the C₁₃-norisoprenoid composition in grapes (Winterhalter and Rouseff 2002, Crupi et al. 2010).

Aromatic Volatile Compounds

Aromatic volatile compounds are compounds that contain a planar, cyclic delocalized π -electron system, and have some detectable odor (Pichersky et al. 2006). Phenylpropanoids and benzenoids are two categories usually found in grape berries and wines. Volatiles in these two categories are important constituents of snapdragon, petunia and rose floral scent in wine (Kolossova et al. 2001, Boatright et al. 2004, Guterman et al. 2006). Phenylpropanoids are compounds with an aromatic six-member ring and a three-carbon chain attached to the ring, such as eugenol (Dudareva et al. 2006). Benzenoids are compounds with a central benzene core and one carbon attached to the ring. The sensory thresholds of the aromatic compounds in grapes appear to be higher than that of other volatile compounds. The sensory threshold of aromatic compounds can vary from low $\mu\text{g/L}$ level to 10mg/L in hydro-alcoholic mixtures (Dunlevy et al., 2009). Some representative aromatic compounds are listed in Table 1.2 with their sensory descriptors and thresholds.

Table 1.2. Odors of some important volatile aromatic compounds

Compounds	Odor descriptor	Odor threshold ($\mu\text{g/L}$) \times
2-Phenylethanol	Honey, rose	10000 [1]
2-Phenylethyl acetate	Honey, rose, tobacco	250 [1]
Guaiacol	Smoky, medicine, sweet	9.5 [1]
4-Ethyl guaiacol	Leather, spice, clove	33 [1]
4-Vinyl guaiacol	Clove, curry	40 [1]
Eugenol	Clove, honey	5 [1]
4-Ethyl phenol	Leather, medicine	440 [1]

m-cresol	Leather, spicy	68 [2]
E-ethyl cinnamate	Cinnamon	1.1 [1]
Methyl anthranilate	Grape juice	3 [3]

Table reference: 1: Aubry et al. 1997, 2: Francis and Newton 2005, 3: Escudero et al. 2007

Among these phenylpropanoids and benzenoids, phenylethyl alcohol and 2-phenylethyl acetate contribute rose, floral and honey aromas to the wine, and are typically found at concentrations (Robinson et al., 2014) above their sensory thresholds (Guth 1997). These two compounds can be traced back to the *Saccharomyces cerevisiae* metabolized aromatic amino acids, including phenylalanine and tyrosine. The ethyl phenols, known for their leather and barnyard characters to wine, are considered detrimental to consumer acceptability (Chatonnet et al. 1992, Lattey et al. 2010). *Brettanomyces* sp. and its ascosporeogenous from *Dekkera* can break down hydroxycinnamic acids to vinyl phenols and subsequently to ethyl phenols (Wedral, Shewfelt et al. 2010). It is reported that volatile phenylpropanoids in wines also can be traced back to oak barrels (Prida and Chatonnet 2010). It is also suggested that phenylpropanoids can be passed onto grapes by exposure to smoke events in the field (Kennison et al., 2008; Hayasaka et al. 2010).

1.1.2 Fermentation-derived volatile compounds

Wine fermentation is a transformation process changing grapes to wine by yeast in an anaerobic environment. It is well understood that the majority of fatty acids, esters and higher alcohols in wine are produced during the fermentation process through sugar and amino acid metabolism (Swiegers et al. 2005, Sumbly et al. 2010). Most active aroma compounds are produced or modified during fermentation. During fermentation, yeasts not only convert sugar to carbon dioxide (CO₂) and ethanol, but also higher alcohols, acids, esters, phenols, aldehydes and volatile sulfurs that contribute to wine aroma. The

synthesis pathway for higher alcohols, esters and acids during fermentation is shown in Figure 1.5

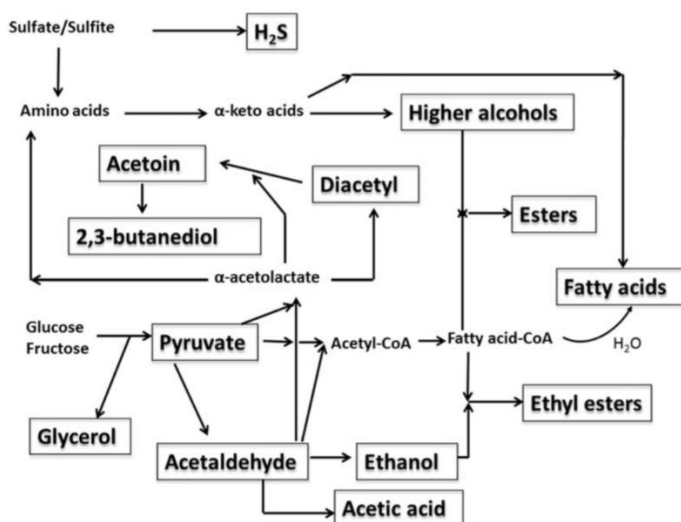


Fig 1.5. The synthesis pathway for higher alcohols, esters and acid in wine
Figure reference: Styger, Prior et al. 2011

Alcohols

Ethanol, generated yeasts by anaerobic fermentation, is the most important alcohol in wine. The ethanol concentration can accumulate up to about 14% to 15% (Jackson 2008). Ethanol acts as an important solvent to extract pigments and tannins in wine, which influence the color and taste. Ethanol itself has multiple effects on wine mouth-feel as well (Lea and Arnold 1978). Furthermore, ethanol is also an essential reactant for the formation of many volatile esters.

Alcohols with more than two carbon atoms are called higher alcohols. They have a characteristic pungent odor (Bakker et al., 2011). At high concentrations (>300mg/L), higher alcohols have negative effects on wine aroma (Bakker and Clarke, 2011). The most common higher alcohols in wine include 1-propanol, 2-methyl-1-propanol (isobutyl alcohol), 3-methyl-1-butanol (isoamyl alcohol) and phenyl ethyl alcohol. 1-propanol contributes a fruity note to wine with a sensory threshold of 9 mg/L in water. The

branched-chain isobutyl alcohol and isoamyl alcohol contribute the wine, solvent, bitter and whiskey, malt and burnt notes to the wine flavor, respectively (Francis and Newton 2005). Phenylethyl alcohol is considered to be one of the most important higher alcohols to wine aroma, as it has a honey, rose and lilac aroma and is typically found at concentrations above its sensory threshold of 10 mg/L in model wine (Guth 1997).

The majority of higher alcohols are produced by *Saccharomyces cerevisiae* from sugar metabolism during fermentation. The generation pathway of higher alcohols is presented in Figure 1.5. The majority of higher alcohols generated from sugar metabolism with α -keto acid serving as precursor. Alternatively, higher alcohols can also be produced by yeast amino acids metabolism (BELL and Henschke 2005, Hernández-Orte et al. 2006; Rossouw et al. 2009). The branched-chain higher alcohols, including isobutyl alcohol and isoamyl alcohol, are synthesized from branched-chain amino acids (valine, leucine, isoleucine, threonine and phenylalanine), the aromatic alcohols, such as Phenylethyl alcohol is generated from aromatic amino acids, including phenylalanine and tyrosine (Rossouw, Olivares-Hernandes et al. 2009). Alternative to this pathway, higher alcohols can also be synthesized from α -keto acid, which serve as an intermediate in cell glucose metabolism (BELL and Henschke 2005, Hernández-Orte, Ibarz et al. 2006). Research has proved that the production of β -phenylethanol and benzyl alcohol increase with the presence of greater concentrations of amino acids (Hernández-Orte, Ibarz et al. 2006). Therefore, amino acid components together with ammonium from the yeast assimilable nitrogen (YAN) in grape berries, is particularly important for yeast growth and the formation of wine aroma compounds (BELL et al., 2005).

The formation of some higher alcohols in wine is related with the YAN level in grapes. However, it is reported that the yeast assimilable nitrogen (YAN) level is associated with nitrogen level in grape vine, which can be altered by viticultural practices, such as nitrogen fertilization (Keller et al., 2005; Schreiner et al., 2013) and soil management techniques (BELL et al., 2005). Thus, the higher alcohol content in wine could be manipulated by viticultural practices in vineyard.

Esters

Esters are the most abundant volatile compounds in alcoholic beverages, mainly responsible for fruity aromas in wine. Two important groups of esters in wine are considered to be acetates and fatty acid ethyl esters, both of which are products of enzymatic reactions during fermentation. Ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl decanoate are considered important fatty acid ethyl esters contributing to wine aroma. Important acetates in wine include ethyl acetate, hexyl acetate, isoamyl acetate, isobutyl acetate and phenethyl acetate (Ferreira et al. 2000, Francis and Newton 2005). High concentrations of ethyl propanoate, ethyl 2-methylpropanoate and ethyl 2-methylbutanoate were reported to contribute to the blackberry aroma in Bordeaux red wines, while ethyl butanoate, ethyl hexanoate, ethyl octanoate and ethyl 3-hydroxybutanoate contributed to red berry aromas to the wines (Pineau et al. 2009). Ferreira et al. (Ferreira et al. 2000) pointed out that, in young Spanish red wines, the most important differences between young wines of different varieties were due to the presence of isoamyl acetate, isovaleric acid and isobutyric acid and their esters. It is also reported that the loss of fruity and floral aromas in young white wines during storage is associated with the loss of esters (Pérez-Coello et al. 2003).

Esters are usually formed by lipid and acetyl-CoA metabolism during fermentation (Saerens et al. 2010). Some esters are generated from the reaction of alcohols and acid at low pH during wine aging (Saerens et al. 2008). As shown in Figure 1.5, grape amino acids may serve as direct precursors of esters, suggesting that the content of amino acids in grape must before fermentation could influence the formation of esters. Hernández-Orte et al (2006) found that isoamyl acetate, β -phenylethyl acetate, ethyl hexanoate, ethyl octanoate increased with additional amino acids in the grape juice before fermentation. However, amino acid supplementation is not always positively correlated with higher ester concentrations in wine (Miller et al., 2007).

Volatile sulfur compounds

Volatile sulfur compounds are a diverse group of highly odor-active sulfur-containing compounds with multiple influences contributing to wine flavors. Various sulfur compounds, including the simple alkyl thiols and complex thiolactones and terpene thiols (Bakker and Clarke 2011) have been identified in wines, ranging from below trace amounts 1 ng/L to over 10mg/L (Mestres et al. 2000). Volatile sulfur compounds produce a variety of aromas in wine, both negative (e.g. hydrogen sulfide (H₂S) with a rotten egg aroma) and positive (e.g. 3-mercaptohexan-1-yl acetate with tropical and citrus fruit flavor).

The most abundant volatile sulfur compounds in wines are hydrogen sulfide, methanethiol, dimethyl mercaptans [including dimethyl sulfide (DMS), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS)], methylthio-esters (including methyl thioacetate (MeSoAc), methyl thiopropanoate and methyl thiobutanoate) and liberated glutathione and cysteine polyfunctional thiols [including 3-Mercaptohexan-1-ol (3MH), 3-mercaptohexylacetate (3MHA) and 4-methyl-4-mercaptopentan-2-one (4MMP)]. H₂S is the most extensively studied volatile sulfur compound in wine, because of its off-flavor of rotten egg (Moreira et al., 2002). It is well accepted that the majority of H₂S emerges as an intermediate product in the biosynthesis of sulfur-containing amino acids by yeast during fermentation (Dunlevy, 2009). A negative correlation between naturally occurring nitrogen in grape must and total H₂S in wine has been found (Vos and Gray, 1979).

Studies have shown that DMS can increase black olive and truffle notes in Syrah wines (Segurel et al. 2004). DMS can also enhance the fruit aroma of red wines via interactions with esters and norisoprenoids (Escudero et al. 2007). Methionol presents a raw potato or cauliflower note to wine, and it is believed to contribute to the cooked vegetable aroma of oxidized wines (Escudero et al. 2000). Methyl mercaptan (MeSH), ethyl mercaptan (EtSH), DMS, and diethyl disulfide (DEDS) have been reported as potential contributors to wine aroma (He et al. 2013; Herszage and Ebeler 2011), and, at very low levels, may enhance the fruity aromas in wine (Escudero et al. 2007; Segurel et al. 2004).

1.1.3 Compounds generated during aging

The aging of wine is believed to have influence on the wine quality by altering the aroma, color, mouthfeel and taste of wine. Most wines achieve better quality with aging for a few months to years before showing irreversible loss of quality (Jackson, 2008). However, Syrah, Pinot noir, Tempranillo, and Cabernet Sauvignon may continue to improve their flavors and tastes for decades (Jackson, 2008). Generally, the aging of wines leads to a loss of the characteristic fresh and fruity aromas linked to the grape, and generates new aromas. Volatile esters, especially straight-chain fatty acids and fusel alcohol acetates, produced during fermentation are primarily responsible for the fresh and fruity character of young wines (Van der Merwe, 1981). Volatile esters that related with fruity notes in young wines showed decreasing trend during wine aging (Garofolo, 1994; Shinohara, 1981). However, ethyl esters of branched-chain fatty acids are stable or even increase during wine aging (Díaz-Maroto et al., 2005).

It is also found that aging of wine with residual yeast decreases volatile contents related to fruity aroma and increases long-chain alcohols and volatile fatty acids (Pérez-Serradilla et al., 2008). Except for esters, monoterpene alcohols drop markedly during wine aging (Jackson, 2008). The autolysis and liberated fatty acids from lipids are responsible for the rise of aldehyde and ketone concentrations in aging wine (Pueyo et al., 2000). Additionally, the physical structure and chemical composition of the barrels will also change the composition of wine during aging (Ferreira, 2006; Jarauta, 2005).

1.2. The impact of deficit irrigation on grape and wine

It is well known that accurate control of water deficit is necessary to obtain high quality grapes for premium wine production (Ojeda et al. 2002, Pellegrino et al. 2005). Previous studies showed that changes in grapevine water status have a direct effect on grape composition through influencing vegetative growth, yield, canopy microclimate, and fruit metabolism in the grapevine (Dry and Loveys 1998, Pellegrino et al. 2005,

Ezzhaouani et al. 2007). In general, moderate water deficits were shown to have a positive impact on wine quality in red wine grape varieties (Bravdo et al. 1985).

Regulated deficit irrigation (RDI) is a common vineyard water management techniques that control the application of a period of mild water stress to grapevines between fruit set and veraison. Regulated deficit irrigation can control vegetative growth without negatively affecting production by providing planned water deficits at specific crop developmental stages (Kriedemann and Goodwin 2003). RDI can improve fruit quality through decreasing yield and berry size (Pellegrino et al. 2005, Acevedo-Opazo et al. 2010). However, the effects of deficit irrigation on berry and wine quality also depends on other factors, including the climatic characteristics during the growing season, soil type, grapevine variety and timing of application (Schultz 1995, Dry and Loveys 1998; Lovisolo et al. 2010).

The success of RDI is closely related to the time when water restriction is applied to the grapevine during grape development. Water restriction applied in the different stages of grapevine development show different effects on grapes (Acevedo-Opazo, 2010). When RDI is applied during canopy development stage (Figure 1.6), it might cause an insufficient leaf area after veraison, which leads to the reduction of sugar synthesis and sun damage to grape berries (Weeks, C et al., 1984). The implementation of RDI during flowering reduces yield due to the abscission and desiccation of flowers (Hardie and Considine 1976). Between fruit setting and veraison, RDI significantly reduces grapevine vigor while partially reducing the yield (Goodwin and Macrae 1990). However, the implementation of RDI at the final stage between veraison and harvest has no significant effects on yield (Goodwin and Macrae, 1990).

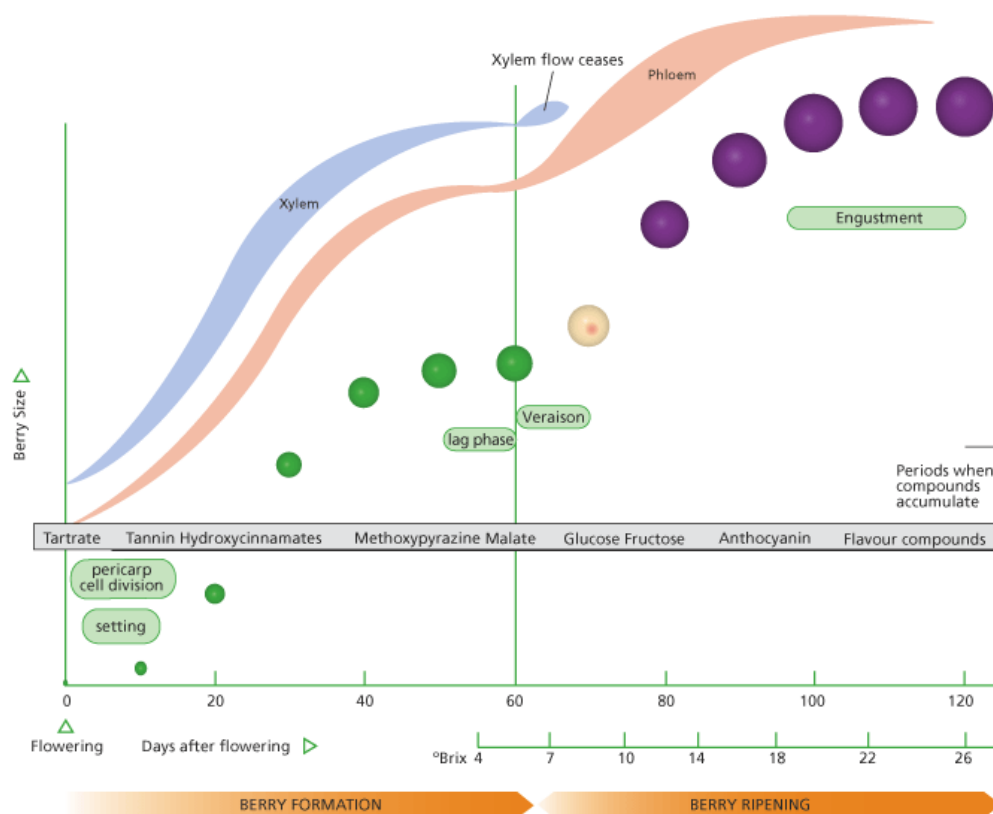


Figure 1.6 The change of size and color of grapes in different stages (Coombe et al. 2000)

The climate also has impacts on grape berry quality. Leaves exposed to constant strong light, high temperature lead to the photoinhibition of grapevines, leading the maximum quantum efficiency of PSII slightly declines at midday, which will cause the accumulation of soluble sugars (Lovisolò et al., 2010). The accumulation of soluble sugars then inhibits the photosynthesis. As shown on Figure 1.7, the formation of polyphenols, flavors and anthocyanins can be traced back to ABA and sugar flux. When water deficit occurring at pre-veraison, cell turgor is lowered, which induces an increase in sugar influx and ABA, influencing several key steps of the phenylpropanoid biosynthetic pathway, and eventually influence the generation of polyphenols, flavors and anthocyanins (Lovisolò et al., 2010).

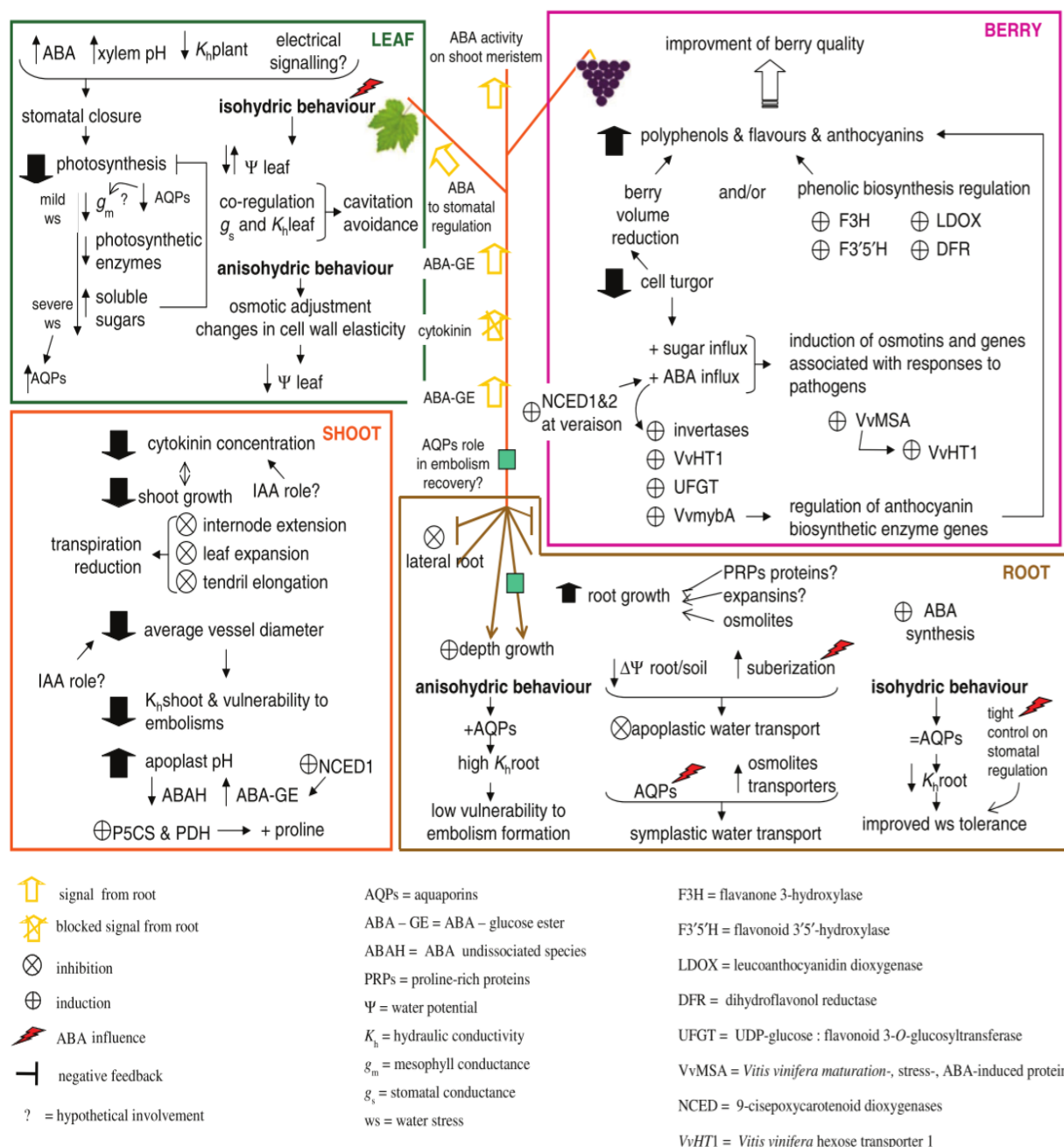


Fig. 1.7. Summary of water stress effects on grapevine root, shoot, leaf and berry (Lovisol et al. 2010)

Soil water availability and soil hydraulic conductivity are the two main factors of soil that can influence deficit irrigation efficiency (Acevedo-Opazo et al. 2010). Water and nutrients are closely related since all nutrients are dissolved in soil water. The soil

type can influence the content of dissolved nutrients, which influence grapevine development and berries ripening through mineral supply (Keller 2005).

Studies conducted on impact of water deficit on berry metabolism and composition changes have been mainly focused on synthesis and concentration of phenolic compounds, soluble solids, and anthocyanins in grape berries (Ginestar et al. 1998, Kennedy et al. 2002, Ojeda et al. 2002). It is reported that small water supplements might increase yields and improve grape berry quality (Matthews and Anderson 1989, dos Santos et al. 2003, Santos et al. 2007). Excessive irrigation results in a negative impact on grape sugar content and pigment, which will eventually affect the wine aroma (Bravdo et al. 1985, Esteban et al. 2001, Chalmers et al. 2010). The application of RDI has shown to have positive influences on berry quality of Merlot, Cabernet Sauvignon, by decreasing yield and berry size, leading to increased concentrations of phenolic compounds, total soluble solids and anthocyanins (Ojeda et al. 2002, Peterlunger et al. 2002, Roby et al. 2004, Deluc et al. 2009). However, Jerie and Goodwin (2002) found that the grape berries of vines under severe RDI condition accumulate lower soluble solids.

Vine water stress has been associated with greater concentrations of glycol-conjugates of some main aroma components of grapes (Bravdo and Shoseyov 2000, Koundouras et al. 2006). The influence of irrigation strategy on grape berry aromas has not received much attention. Deficit irrigation during the growth period has been shown to alter the sensory profile of wine (Matthews et al. 1990). Koundouras et al. (2006) found that wines produced from grapes of stressed vineyards are generally preferred. Wine produced from water stressed berries of Cabernet Sauvignon had significantly higher red/blackberry, jam/cooked berry, dried fruit/raisin, and fruity aromas than wines from well-watered treatments, while wines from well-watered vines had significantly higher vegetal, bell pepper, and black pepper aromas (Chapman et al. 2005). In general, moderate water stress improves wine quality. However, the detailed chemical compounds related to the different flavor attributes in wine needed to be further investigated (Qian and Fang, 2009).

Grape-originated aromas are important contributors to wine flavor, especially young wines (Ribéreau-Gayon et al. 2006). In grapes, only a small portion of volatile

compounds are present as free-form, whereas the majority exist as non-volatile, bound forms or other precursors (Gunata et al. 1985, Winterhalter et al. 1990). These non-volatile aroma precursors can be converted to aroma-active compounds through enzymatic or chemical hydrolysis during fermentation and aging, which can significantly affect overall wine aroma (López et al. 2004). As plant secondary metabolites, the synthesis of grape-derived volatile compounds could be affected by viticultural practices (Robinson et al. 2013) and consequently affect the volatile composition of wines. Many researches demonstrated that reduced vine water availability through vineyard deficit irrigation could increase the levels of bound terpenoids and C₁₃-norisoprenoids, leading to final wines with less vegetative and fruitier aromas (Koundouras et al. 2009, Qian and Fang, 2009, Ou et al. 2010, Song et al. 2012). Terpenoids and C₁₃-norisoprenoids are important grape derived-aroma that contribute to floral, fruity and berry flavor in the wine. However, there is still information missing on many important aroma compounds. Moreover, the response of grapevines to regulated irrigation is also affected by other factors such as irrigation application time and stress levels. Vineyard location and site is of utmost importance but little research relative to irrigation has been published under similar conditions. By studying the impact of RDI on grape aroma development, we aimed to have a better understanding of region-specific RDI and possible enhancement of grape-derived aromas in wine production of Idaho.

1.3 Justification of Research

It is well known that accurate control of water deficits is necessary to obtain high quality grapes for wine production (Ojeda et al., 2002; Pellegrino et al., 2005). The aroma of wine is one of the key factors that determine customer acceptance of wine. The quality of wine depends on many factors, including the fermentation process and wine aging, but most importantly, grape quality. It is well accepted that premium wine can only be made from high quality grapes. The quality of grapes can be influenced by environment factors and vineyard management practices. Since environment factors are dictated by the

location of the vineyard, vineyard practices are the most important tools for growers to obtain high quality wine grapes.

Water deficit irrigation is already a commercial practice used in the production of red wine grapes in many regions to enhance water use efficiency. Imposing a water deficit to the vine during berry development is an important vineyard management strategy to alter grape and final wine quality. The effect of vine water status on grape-derived volatiles and their precursors in grape and wine has been well studied (Bindon et al., 2007; Kennedy et al., 2006; Koundouras, et al., 2009; Koundouras et al., 2006). It is reported that moderate water deficit can alter the wine aroma (D. M. Chapman et al., 2005; Koundouras et al., 2006; Qian et al., 2009). However, severe water deficit has a negative effect on grape quality, which will eventually influence wine quality. The results of water deficit are still inconclusive since the enormous variations in irrigation environments, cultivars and other agronomical conditions. The detailed chemical compounds responsible for the flavor attributes difference from different wine need to be fully studied.

The overall hypothesis of this dissertation is that grape-derived volatile compounds can be modified by viticulture water management in vineyard and eventually alter the wine volatile composition.

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**CHAPTER 2 WATER MANAGEMENT ON GRAPEVINES: EFFECT OF
DEFICIT IRRIGATION ON MALBEC AND SYRAH GRAPE COMPOSITION**

Xiaoxi Yuan^a, Yanping Qian^a, Krista Shellie^b, Michael C. Qian^{a*}

^a Department of Food Science and Technology, Oregon State University, Corvallis, OR
97331

^b Agricultural Research Service, Horticultural Crops Research Laboratory, US
Department of Agriculture, 29603 U of I Lane, Parma, ID 83660

*Corresponding author: Michael Qian. phone: 541-737-9114, fax: 541-737-1877, email:

Michael.Qian@oregonstate.edu

2.1 Abstract

The impact of regulated deficit irrigation during berry development on Malbec and Syrah grape volatile composition was evaluated. Ungrafted (self-rooted) Malbec and Syrah vines were supplied with eight different deficit irrigation treatments [70 or 35% crop evapotranspiration (ET_c) sustained from fruit set to harvest, 35% ET_c increased to 70% ET_c at veraison, or 70% ET_c decreased to 35% ET_c at veraison as the main factor and irrigation frequency 3 or 7 days as subplots] throughout berry development. Volatiles were analyzed using the SPME-GC-MS technique. The results showed that the effect of regulated deficit irrigation was dependent on grape variety. C₆ compounds were not influenced by irrigation frequency or amount in both Malbec and Syrah. Both irrigation frequency and irrigation amount showed no influence on C₁₃-norisoprenoids concentration in Malbec berries, however, C₁₃-norisoprenoid in Syrah were affected by the irrigation frequency and amount. Bound form of TDN and vitispirane were higher in 1-day irrigation frequency and 35/35 irrigation amount of Syrah grapes. Free terpenes in both Malbec and Syrah grapes were all below their sensory thresholds. Irrigation amount showed no impact on bound-form C₁₃-norisoprenoids in Malbec grapes, but 35% ET_c sustained from fruit set to harvest treatment led to higher bound-form TDN and vitispirane concentrations in Syrah.

Key words: regulated deficit irrigation, Syrah, Malbec, grape volatiles, YAN, SPME

2.2 Introduction

Wine is a complex alcoholic beverage in which its flavor compounds are derived from multiple origins (Ebeler and Thorngate, 2009; González-Álvarez et al., 2013). It is well accepted that the grape is one of the most influential determinants of wine quality, and premium wine can only be made from high quality grapes, so efforts have been made to improve grape quality by vineyard management. Environmental factors and viticultural practices are the major two factors that can influence the quality of grapes (Jackson and Lombard, 1993). Since the environmental factors have been decided by the vineyard location, viticultural practices become the major source for growers to achieve desired grape quality.

It is well known that accurate control of water deficits is necessary to obtain high quality grapes for wine production (Ojeda et al., 2002; Pellegrino et al., 2005). Water status during berry development will directly affect vine physiology, and secondary metabolism of the plant (Qian et al., 2009). The water status of wine grapes throughout the growing season is a primary determinant of vine vigor and berry composition, which eventually influence wine quality (Matthews et al., 1990). Previous studies have shown that water deficit can influence physiological parameters of grape vine (Iacono et al., 1998), change berry composition (Bindon et al., 2008; Esteban et al., 1999; Esteban et al., 2001) and improve wine sensory (Chapman et al., 2005; Qian et al., 2009). Deluc and Quilici (2009) found that water deficit showed significant impact on the abundance of some transcripts and metabolites involved in phenylpropanoid, isoprenoid, carotenoid, amino acid and fatty acid metabolism in Cabernet Sauvignon and Chardonnay berries. C₁₃-norisoprenoids, especially β -damascenone and β -ionone, have been identified in wines as an important volatile compound, which can be traced back to the C₁₃-norisoprenoids precursors in grapes. Under water deficit conditions, the concentrations of C₁₃-norisoprenoids and glycoside-bonded volatile compounds can be increased (K. A. Bindon et al., 2007; Koundouras et al., 2006). The impact of vine water status during berry development on the wine aroma profile of Merlot has been investigated by Qian's

group (Song et al., 2012). It has been observed that deficit irrigation during berry development had a consistent effect on the volatile composition of the Merlot wine, especially on C₁₃ norisoprenoids (Song et al., 2012). Although much literature has reported the effect of vine water status on grape derived volatiles and their precursors (K. A. Bindon et al., 2007; Kennedy et al., 2006; Koundouras et al., 2009; Koundouras et al., 2006), research is still needed on deficit irrigation on wine grapes due to the difference among grape cultivars. The detailed study of detailed volatile compounds in each grape cultivar and their response to water status are needed.

Except the volatile compounds, the involatile compositions in grapes are reported to be influenced by water deficit as well. The total soluble solids, fresh berry weight, titratable acidity and total phenolic composition in grapes can be altered by the water status of vine (Ginestar et al. 1998, Kennedy et al. 2002, Ojeda et al. 2002). What's more, the amino-N content in grape has been reported to have implications for wine quality. Some amino acids are involved in the formation of some aroma compounds in wine, including some important esters and higher alcohols (Rapp and Versini, 1991; Hernández-Orte, 2002; Hernández-Orte, 2006). Some evidence suggests that yeast assimilable nitrogen (YAN) level in grape must is sensitive to the availability of vine water (Jackson and Lombard, 1993; Keller, 2005; Peyrot de Gachons et al. 2005; Okamoto et al. 2001, 2004). However, the relationship between water status and the YAN content in grape juice is complex, and the interaction of different degree of water deficit and YAN content in grape is a knowledge gap. Thus, the objective of this study was to investigate influence of vine water deficit on Malbec and Syrah grape quality.

2.3 Materials and Methods

2.3.1 Chemicals

All chemicals were of analytical reagent grade unless stated. Water was obtained from a Milli-Q purification system (Millipore, North Ryde, NSW, Australia). (E)-2-Hexanal (95%), hexanol (99%), α -terpineol (90%), β -damascenone ($\geq 90\%$), benzyl alcohol (99.8%), benzene ethanol (99%), β -ionone (95%), 1-octanol ($\geq 99\%$), linalool

(97%), linalool oxide (mixture of isomers, $\geq 97\%$), 2-ethyl-hexanol ($\geq 96\%$), 1-octen-3-ol (98%), β -citronellol (95%), geraniol (98%) and hexanoic acid (99%) were purchased from Sigma-Aldrich (St. Louis, MO). Hexanal was purchased from ICN Biochemicals (Irvine, CA). Methanol was purchased from EMD (GC grade, Gibbstown, NJ). Citric acid ($>99.0\%$) was purchased from Lancaster (Ward Hill, MA). Sodium chloride was obtained from Fisher Scientific (Fair Lawn, NJ).

2.3.2 Vineyard experimental design

Vineyard

The research was conducted over three consecutive growing seasons (2014-2017) in established field trials located at the University of Idaho Parma Research and Extension Center in Parma, ID (lat: 43°78'N; long: 116°94'W; 750 m asl). The soil (sandy loam, available water-holding capacity of 0.14 cm/cm soil), climatic conditions (semi-arid, dry steppe with warmest monthly average temperature of 32°C), and irrigation water supplied (well water with sand media filter) at this location were well-suited for conducting deficit irrigation field research. The research was conducted in an irrigation trial that was planted in 2007 with the wine grape cultivars Malbec and Syrah. The vines in both trials were ungrafted (own-rooted), irrigated by above ground drip, and grown with the same training and trellis system (double-trunked, bilateral cordon, spur-pruned annually to 16 buds/m of cordon, vertical shoot positioned on a two-wire trellis with moveable wind wires). Vine water demand (crop evapotranspiration, ET_c) was estimated weekly using the 1982 Kimberly–Penman equation with alfalfa as a reference crop obtained from a local weather station (Agrimet) and a variable crop coefficient (0.3 to 0.7). Vineyard management reflected local commercial production practices including weed removal and periodic application of pesticides.

Experimental design and treatments

The 'Malbec' and 'Syrah' trials were located adjacent to one another and have the same vine by row spacing (1.8 x 2.4 m) and experimental design [split-plot with irrigation amount (70 or 35% ETC sustained from fruit set to harvest, 35 increased to 70% at veraison, or 70 decreased to 35% at veraison) as the main factor and irrigation frequency (3 or 7d) as subplots]. The irrigation treatments were shown on Table 2.1. Each plot contained 18 vines (three rows of six vines per row) with inner and outer rows considered borders. Replicate plots of each treatment level were plumbed together with independent flow meters and water supply control. Each trial perimeter contained two border vine rows under independent irrigation supply and control.

2.3.3 Determination of berry chemical composition

Fruit samples were harvested from all plots. After harvest, grapes were transported to the lab in Corvallis, OR and stored at -24 °C for further analysis.

Determination of berry fresh weight, sugar and pH

Sample preparation and analysis followed the procedures of Shellie and Glenn (2008). Individual berry weight was measured by the weight of 100 berries. Total soluble solids (TSS) was measured as °Brix using a digital refractometer. Juice pH was measured with a pH meter (OAKTON, Vernon Hills, IL)

Free -Form volatile compound analysis by SPME-GC MS

Grape was first blended with liquid nitrogen to get grape powder. Grape powder (2g) was diluted with 8 mL of citrate/saturated sodium chloride buffer (0.2M, pH 3.5) in a 20 mL auto-sampler vial. Then 20 µL of internal standard (4-octanol, 10 mg/L) was spiked into the vial, and the cap was tightly capped with a Teflon-faced silicone septa. The volatiles in headspace were extracted by a 2cm-50/30µm DVB/CAR/PDMS fiber (Supelco, Bellefonte, PA). The extraction and injection was conducted by autosampler

(Gerstel, Linthicum, MD). Samples were first equilibrated at 50 °C in a thermostatic bath for 30 min and then extracted by SPME fiber for 30 min at the same temperature with stirring (500 rpm). After extraction, the fiber was inserted into the injection port of GC to desorb the analytes. The injection was performed in the splitless mode and held at 250 °C. The analysis was performed on an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector (Agilent Technologies, Santa Clara, CA). Compound separation was achieved using a ZB-WAX-PLUS column (30 m × 0.25 mm i.d., 0.5 µm film thickness, Phenomenex, Torrance, CA). The column initial temperature was 35 °C, which was held for 4 min and then raised to 230 °C at 4 °C/min, and held at 230 °C for 10 min. The carrier gas was helium with a flow rate of 1.5 mL/min and MS transfer line and ion source temperature were 280°C and 230°C, respectively. Electron ionization mass spectrometric data from m/z 40~350 were collected using a scan mode with an ionization voltage of 70 eV. Compound identification was achieved by comparing retention time with standard compounds and comparing mass spectral data from the Wiley 275.L (G1035) database (Agilent Technologies, Santa Clara, CA).

C₁₃-norisoprenoids potential analysis by SPME-GC MS

Two grams of blended grape powder was mixed with 8 mL of citrate buffer (0.2 M, pH 2.5) and 20 µL of internal standard (4-octanol, 10 mg/L) in a 20ml-autosampler vial, then tightly capped. The sample vials then were incubated in a 99 °C water bath for 1 hour. After incubation, the vial was cooled to room temperature for analysis. The samples analyzed using the same SPME-GC-MS procedure as for free -form volatile compound analysis.

YAN measurement

YAN of the must was measured as the sum of primary amino nitrogen and ammonia nitrogen. Primary nitrogen was measured using the method of Dukes and Butzke (1998). The ammonia nitrogen was measured using a commercial ammonia kit (R-biopharm, Cat. No. 11112732035).

Calibration curves

For the SPME-GC-MS method as previously described, internal standard calibration curve was obtained by the interpolation of relative peak areas in the calibration graphs built by the analysis of synthetic wine (3.5 g/L tartaric acid, 12% v/v ethanol, pH 3.5) containing known amounts of the analytes. Standard calibration curves were obtained through Chemstation software (Agilent Technologies, Santa Clara, CA). Standard calibration curves for each compound were set up by Chemstation, and were used to calculate the concentrations of corresponding volatile compounds in the samples.

2.3.4 Statistical Analysis

Mean values were calculated, treatment differences and interactions were analyzed using analysis of variance (ANOVA) with irrigation amount and irrigation frequency as the main factors using SPSS version 20 (IBM, Chicago, IL). Statistical differences among treatment levels were identified using Tukey's HSD mean separation at the $p < 0.05$ level.

2.4 Results

2.4.1 Grape maturity parameters

The influence of irrigation amount and irrigation frequency on berry weight, total soluble solids (TSS) and pH are shown in Table 2.1 and 2.2. Irrigation amount and irrigation frequency had no impact on the pH and berry weight of Syrah berries. The total soluble solids concentration levels were not influenced by the different irrigation treatments in 2014 and 2016, but this did not consistent in 2015, during which grapes from the 35/35 irrigation amount had higher accumulated TSS. For Malbec grapes, no differences were shown between the two irrigation frequencies. However, the irrigation amount influenced the pH, TSS and berry weight of Malbec grapes. For Malbec juice pH, 35/70 and 35/35 irrigation amount had a relatively higher pH compared to 70/35 and 70/70 irrigation amount in 2014 and 2016. The TSS in 70/70 irrigation amount was high

compared with other treatments in both 2014 and 2015, but this trend was not consistent in 2016. The difference of pH, TSS and berry weight of Malbec among three years were significant, while the pH level of Syrah grapes was not significant among three years.

2.4.2 YAN in grapes must

Table 2.10 and 2.11 showed the YAN content in the grape juice before fermentation. Irrigation frequency showed no influence on the YAN content in either Malbec or Syrah must before fermentation. Irrigation amount showed no impact on the YAN level in either variety in 2014 or in Malbec in 2015. However, in 2016, the 70/70 treatments resulted in a lower level of YAN, while the 35/35 irrigation treatment contributed to a higher YAN content. Among the eight treatments, the 70/70, 3× led to the lowest YAN concentration. This result was consistent in Syrah grapes. Compared to the 35/35 irrigation treatment, the YAN concentration in 70/70 and 70/35 irrigation treatment were significantly lower than the other two treatments. The 70/70, 3× treatment led to the lowest YAN level among the eight different irrigation treatments, while the 35/35, 3× treatment showed the highest YAN concentration in both 2015 and 2016.

2.4.3 Grape volatile composition

Important free aroma active compounds, including C₆ compounds, terpenoids, C₁₃-norisoprenoids and some other compounds were quantified in Syrah and Malbec grape harvested in each growing season (Table 2.7 and 2.8).

C₆ Compounds

Comparing Syrah and Malbec grapes, Syrah showed a higher level of C₆ compounds. For both Malbec and Syrah, as shown on Table 2.2 and Table 2.3, the C₆ compounds showed significant difference among 2014, 2015 and 2016. For 2014, 2015 and 2016 growing seasons, the impact of vineyard water management on C₆ volatile composition were significantly different between Malbec and Syrah. For Syrah grapes in individual years, the 35/35 treatments (both 35/35 1× and 35/35, 3×) showed a higher

level of hexanol in 2014 and a higher hexanal in Syrah grapes of year 2016. Among the C₆ compounds that had been quantified, the C₆ aldehyde level of Malbec were influenced by the irrigation amount, but the impacts of irrigation amount on these compounds was year dependent. The 35/35 irrigation amount led to the highest E-2-hexenal in 2014 and 2015, 70/70 showed less E-2-hexenal in both 2014 and 2015.

Terpenes

Six terpenes were determined in Malbec and Syrah grape berries in this study, including five monoterpenes, linalool, β -citronellol, nerol, geraniol, α -terpineol and one monoterpene ether linalool oxide. Similar to C₆ compounds, the concentration of terpenoids were statistically different among three years. The terpenoid levels were lowest in 2014, during which linalool oxide, linalool, β -citronellol and nerol could not be detected. For Malbec, irrigation frequency showed no difference between treatments for cis-linalool oxide, linalool, β -citronellol, nerol and geraniol, while 3 \times irrigation frequency contributed to a higher level of free α -terpineol in Malbec grape berries. The irrigation amount showed an impact on geraniol and α -terpineol levels. The 35/70 irrigation amount led to the lowest geraniol level in the three growing seasons, while 35/35 irrigation amount contributed to higher geraniol concentrations. The results were consistent for the three growing seasons. Among three years, the average concentration of geraniol in 2015 was 14 $\mu\text{g/L}$, which was higher than that in 2014 and 2016. For α -terpineol, 2014, 2015 and 2016 all showed consistent trend that the 70/70 irrigation amount resulted in the highest α -terpineol concentration level in Malbec. Unlike Malbec, irrigation frequency affected the β -citronellol, nerol, and α -terpineol concentration in Syrah berries. 3 \times irrigation caused higher α -terpineol, but lower β -citronellol and nerol levels. The irrigation amount only influenced the concentration of nerol. The 70/70 and 35/70 treatment resulted in the higher nerol concentration level.

C₁₃-norisoprenoids

The C₁₃-norisoprenoids, including trans- β -damascenone, β -ionone, TDN and vitispirane, were analyzed as free form and after acid hydrolysis. Concentrations of free form and total C₁₃-norisoprenoids after acid hydrolysis are shown in Table 2.6, 2.7 and 2.8. Among the four C₁₃-norisoprenoids quantified, vitispirane and TDN could only be

detected after acid hydrolysis as the bound form. For both Malbec and Syrah, the level of total β -damascenone were significantly different among the three growing seasons. In 2016, the concentration of total β -damascenone in Malbec was the highest, with an average concentration of 15.3 $\mu\text{g/L}$, while in 2015 the bound form β -damascenone was the lowest, at only 8.7 $\mu\text{g/L}$. The total trans- β -damascenone concentration of Syrah was the same in Malbec. As shown on Table 2.3 and 2.4, among 2014, 2015 and 2016, the concentration of total trans- β -damascenone was not significant between treatments within each year for both Malbec and Syrah grapes. The comparison between treatment of different water deficit timing before veraison and after veraison are shown on Table 2.4. For water deficit timing, compared to 35% ETc from fruit to veraison treatments, the 70% ETc from fruit set to veraison showed higher total trans- β -damascenone concentration than 35% ETc in Malbec grapes of both 2015 and 2016 ($p\text{-value}<0.05$). However, no difference was found between 70% ETc and 35% ETc before veraison for Syrah grapes. For Malbec, total trans- β -damascenone, β -ionone, TDN and vitispirane levels (Table 2.3) were not affected by irrigation amount and irrigation frequency. The irrigation frequency and amount did not influence the total trans- β -damascenone, β -ionone and TDN levels in Syrah, but the 3 \times irrigation frequency led to a higher total vitispirane concentration ($p\text{-value}<0.05$). For total vitispirane and TDN in Syrah, 35% ETc before or after veraison all led to the relatively lower level of total vitispirane and TDN compared to 70% ETc (Table 2.5).

Miscellaneous

Other compounds such as alcohols and acids were also identified in Malbec and Syrah grapes. According to Tables 2.3a and 2.3b, benzyl alcohol and hexanoic acid in Malbec grapes with 3 \times irrigation frequency showed a significantly higher concentration. 1-octanol was consistently high in the 70/35 irrigation amount. Benzyl alcohol reached a high level in the 70/35 and 35/35 treatments. The highest hexanoic acid concentration was found in the 35/35 treatment in all three years. For Syrah grapes, phenylethyl alcohol and hexanoic acid concentration were high in 1 \times irrigation frequency (Table 2.3a). The 70/35 treatment had a high 1-octanol concentration in 2014 and 2016, but not in 2015. 1-

octen-3-ol showed a higher concentration in Syrah grapes from 35/70 irrigation amount treatment (Table 2.3b).

2.5 Discussion

It is known that before veraison, grape berries undergo cellular division and enlargement, during which organic acids accumulate. Water deficit in this period will lead to a decreased canopy size. In this study, Malbec berries in 2014 and 2015 of 70% ETc before veraison had larger fresh berry weight than 35% ETc treatments, this might be because the 35% ETc irrigation treatment limited the berry growth before veraison and reduced cell expansion (McCarthy, 1997), which was in agreement with McCarthy (1997), who showed that early season water deficit reduced the berry weight of Cabernet Franc berries. McCarthy (1997) conducted a 4-year study in Shiraz, pointing that water deficit between flowering and veraison reduced the berry size, while after veraison the Syrah became relatively insensitive to soil water deficit. However, in my study, this trend was not observed. This might be due to the different temperature summation, soil type and rainfall differences between the two research plots. The 35/70 and 35/35 treatments had a relatively higher pH in Malbec compared to 70/35 and 70/70 treatments in 2014 and 2016, which was in agreement with previous reports that the water deficit increase pH level (Koundouras et al., 2006), this is most likely due to a reduction in malic acid in grape berries (Koundouras et al., 2006; Song et al., 2012). The TSS in the 70/70 treatments was high compared to other treatments in both 2014 and 2015 in Malbec. It was reported that the RDI applied during canopy development stage will cause a reduction of leaf area. The insufficient leaf area after veraison would lead to the reduction of sugar synthesis rate and sun damages in the grape berries (Weeks. C et.al, 1984). Severe stress (35% ETc) most likely caused a decrease in photosynthesis which led to a reduction in berry sugar accumulation (Quick, 1992; Rogiers et al., 2004). Unlike Malbec, TSS in Syrah were not influenced by different degree of water deficit in 2014 and 2016, this might because of different grape varieties have various tolerances that Syrah is less effected by water stress (Keller, 2005).

The nitrogen-containing compounds in grape could influence the fermentation rate and fermentation-derived volatile composition in wine since the nitrogen compounds can influence the growth and amino acid metabolism of yeast. Yeast assimilable nitrogen (YAN) represent the nitrogen level in grapes, the main sources of YAN were free amino acids and ammonium. The YAN were reported to be sensitive to vine water restrictions (Keller 2005; Chaves et al., 2010). More severe of water deficit has been linked with higher YAN content in grape must in this study. 70% ETc sustained from fruit set to harvest contributed to higher YAN level in grape must, while 35/35 ETc was the lowest. This finding was in agreement with K.D. Hannam's (2102) results in Merlot grapes and Wade's (2004) reports on Shiraz that YAN status improved with reduced irrigation. Peyrot des Gachons et al. (2005) also noticed that the total N concentrations of Sauvignon Blanc in France were higher on the driest site, and was further increased by strong water deficit. This finding was similar to our results in Syrah and Malbec.

Originated from fatty acid oxidation and amino acid degradation, C₆ compounds contribute the green and herbaceous aroma in grape and wine. The important C₆ compounds include C₆-alcohols and C₆-aldehydes. The C₆ compounds are the most abundant aroma-active compounds quantified in this study, among which, C₆-aldehydes showed high concentrations. Comparing Syrah and Malbec grapes, Syrah showed a higher level of C₆ compounds. The C₆ compounds in this study showed significant difference among three growing seasons. This might be due to the different weather condition in each growing season (Table 2.12a and 2.12b). Overall, in this study, the irrigation frequency showed no impact on C₆ compounds. The impacts of irrigation amount on C₆ compounds on grapes were year dependent, which was in agreement with Song et al. (2012) and Qian results that water status can affect, but inconsistently affected, the accumulation of C₆ compounds in Merlot grapes. This difference might due to the different degree of maturity of the grape berries, since Fang and Qian (2012) reported that the total C₆-aldehyde only decreased at the final stage of grape ripening.

Terpenes contribute floral, fruity and citrus notes to wine aroma (Câmara et al., 2004). Monoterpenes are the dominant terpenes with characteristic floral and fruity aroma. Grapes from Muscat varieties have high free monoterpenes level, which can reach

up to 6 mg/L. Our study found that the 35/70 treatment led to the lowest geraniol level in all three growing seasons, while the 35/35 treatment contribute to the high geraniol concentration in Malbec. The 70/70 treatment resulted in the highest α -terpineol concentration level in Malbec. The 70/70 and 35/70 treatments resulted in the higher nerol concentrations in Syrah. These results were different from Song's (2012) finding that water deficit had no consistent effect on free terpenoids. Regardless, terpenoids in grapes consisted of both free and glycoside-bound form, while the free terpenoids were present in only a small portion (Song et al., 2012).

C₁₃-norisoprenoids are important grape-derived aroma compounds found in wine. The C₁₃-norisoprenoids are usually present as bound form in grape berries, only few can be found in grapes as free form volatiles. The determination of C₁₃-norisoprenoids in grape berries needs hydrolysis to release the bounded C₁₃-norisoprenoids precursors before the analysis. Acid hydrolysis is more efficient for the hydrolysis of the bound form (Loscos et al., 2010). In this study, the C₁₃-norisoprenoids, including trans- β -damascenone, β -ionone, TDN and vitispirane, were analyzed as free form and after acid hydrolysis. After acid hydrolysis, the C₁₃-norisoprenoids levels dramatically increased, indicating that C₁₃-norisoprenoids were existed in grape berries basically as precursors. Among four C₁₃-norisoprenoids quantified in this study, vitispirane and TDN could only be detected after acid hydrolysis. In this study, total vitispirane and TDN in Syrah grapes, 35% ETc applied before or after veraison all led to the relatively lower level of total vitispirane and TDN compared to 70% ETc. which was similar to Song's finding (Song et al., 2012) that the bound TDN concentration were increased with the increase of water deficit level.

Generated from carotenoids, C₁₃-norisoprenoids concentrations were influenced by the carotenoids in grape berries (Kanasawud and Crouzet, 1990; Mendes-Pinto, 2009; Yuan and Qian, 2016). It is reported that the water stress in grapevine could affect the light environment of grapes by reducing shoot growth rate and vine leaf area (Dry and Loveys, 1998), which would potentially influence the metabolism of carotenoids in grape berries. The change in carotenoids influenced the C₁₃-norisoprenoids content in grapes (K. A. Bindon et al., 2007; Deluc, et al., 2009). Studies have shown that light promotes the increase of carotenoids in grapes before veraison, while grapes exposed to sunlight led to

a decrease of carotenoids during maturation (Baumes et al., 2002; Razungles et al., 1996). The higher total trans- β -damascenone in Malbec berries of 70% ET_c from fruit set to veraison stage in 2015 and 2016 might be due to the increase of carotenoids by water stress. However, the Syrah did not show the trend, this could be the influence of that the carotenoid compounds in the mRNA expression patterns in Syrah being affected by the water stress compared with those in Malbec (Deluc et al., 2007).

2.6 Summary

In summary, this research demonstrates the role of deficit irrigation on the aroma compounds profile of Malbec and Syrah. Malbec and Syrah performed differently on irrigation frequency and irrigation amount. No significant difference was found among irrigation amount and frequency on pH and fresh berry weight of Syrah grapes. The 70/35 treatment led to a lower pH compared to rest of the treatments in 2014 and 2016. 70% ET_c sustained from fruit set to harvest irrigation treatment had highest TTS content in 2014 and 2015. No difference among YAN content of different irrigation treatments was found in 2014 growing season for either Malbec or Syrah. However, in 2015's Syrah and 2016's Malbec and Syrah, the 70/70 treatment showed lower YAN content, whereas the 35/35 treatment had the highest YAN level. For volatile compounds, Syrah berries were more sensitive to the irrigation frequency than Malbec, since α -terpineol, β -citronellol, nerol, vitispirane, TDN, Phenylethyl alcohol and hexanoic acid levels in Syrah were all influenced by irrigation frequency, while only α -terpineol, benzyl alcohol and hexanoic acid in Malbec berries were affected by irrigation frequency. Irrigation amount were more influential than irrigation frequency on volatile composition in Malbec and Syrah grape berries. For Malbec, the 70/35 and 35/35 treatments contributed to higher content of E-2-hexenal, α -terpineol, β -citronellol, 1-octanol, 1-octen-3-ol, benzyl alcohol, Phenylethyl alcohol and hexanoic acid. In Syrah berries, 35/35 irrigation amount resulted in highest concentration of TDN and vitispirane. In

general, the irrigation frequency did not show impact on Malbec and Syrah wine quality, but the irrigation amount difference could affect the Malbec and Syrah grape quality.

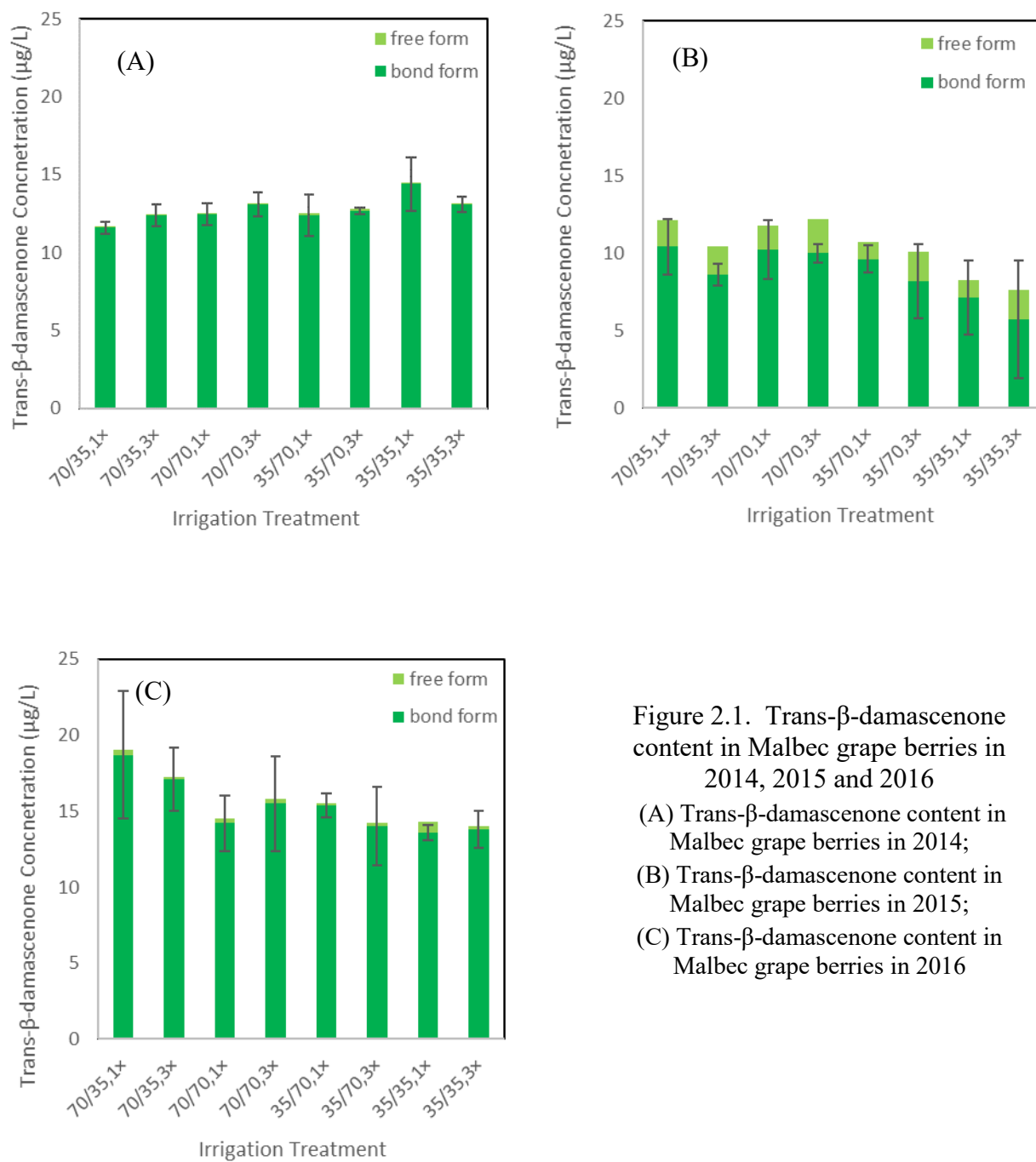


Figure 2.1. Trans-β-damascenone content in Malbec grape berries in 2014, 2015 and 2016

(A) Trans-β-damascenone content in Malbec grape berries in 2014;

(B) Trans-β-damascenone content in Malbec grape berries in 2015;

(C) Trans-β-damascenone content in Malbec grape berries in 2016

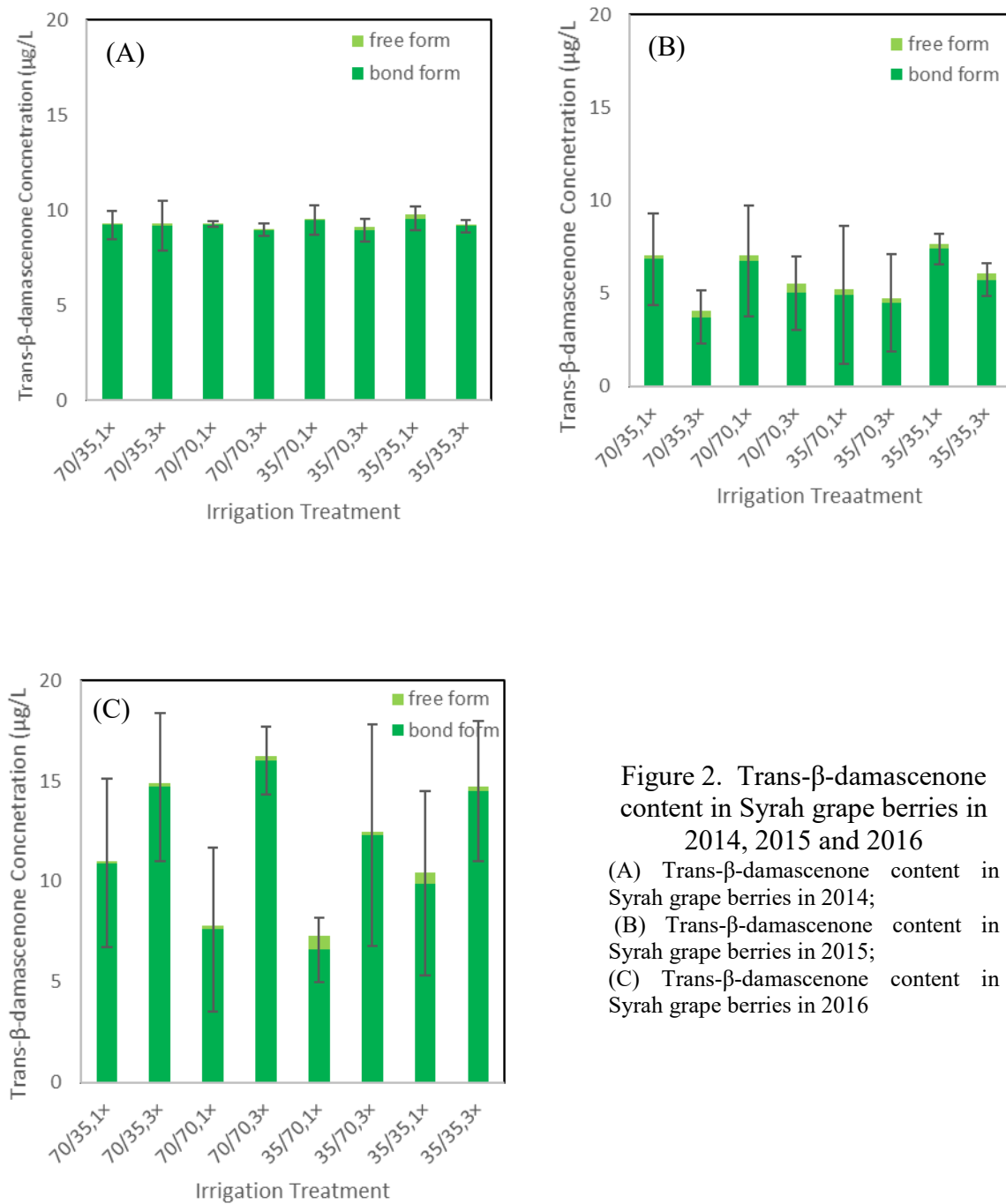


Figure 2. Trans- β -damascenone content in Syrah grape berries in 2014, 2015 and 2016

- (A) Trans- β -damascenone content in Syrah grape berries in 2014;
 (B) Trans- β -damascenone content in Syrah grape berries in 2015;
 (C) Trans- β -damascenone content in Syrah grape berries in 2016

Table 2.1 Experimental Design for the study

Irrigation Treatment	Irrigation frequency	Abbreviation
70% ET fruit set to veraison, 35% ET veraison to harvest	3d	70/35,1×
	7d	70/35,3×
70 % ET fruit set to veraison	3d	70/70,1×
	7d	70/70,3×
35% ET fruit set to veraison, 70% ET veraison to harvest	3d	35/70,1×
	7d	35/70,3×
35% ET fruit set to veraison	3d	35/35,1×
	7d	35/35,3×

Table 2.2 a Basic grape parameter for 2014, 2015 and 2016 harvested Malbec grape

Irrigation Amount	Irrigation Frequency	Juice pH			TSS (Brix)			Berry Weight (g/berry)		
		2014	2015	2016	2014	2015	2016	2014	2015	2016
70/35	1×	3.15 bc	3.43	3.48 c	23.4 c	22.6 abc	22.1	1.38 ab	1.26	1.47
	3×	3.08 c	3.43	3.69 abc	23.5 c	24.9 ab	22.4	1.38 ab	1.32	1.56
70/70	1×	3.17 abc	3.39	3.55 bc	26.7 a	23.5 abc	22.3	1.39 ab	1.39	1.58
	3×	3.13 bc	3.32	3.59 abc	26.2 ab	25.3 a	21.5	1.56 a	1.38	1.7
35/70	1×	3.32 abc	3.41	3.88 a	23.9 bc	21.3 bc	23.2	1.29 ab	1.34	1.63
	3×	3.41 a	3.28	3.85 ab	24.1 bc	20.4 c	23.6	1.25 b	1.19	1.76
35/35	1×	3.24 abc	3.39	3.69 abc	23.4 c	21.7 abc	23.5	1.28 b	1.35	1.67
	3×	3.35 a	3.42	3.7 abc	23.2 c	22.2 abc	23.6	1.15 b	1.22	1.49

Mean values for juice pH, TSS and berry weight. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n=3$ independent field samples). ns, not significant.

Table 2.2b Basic grape parameter for 2014, 2015 and 2016 harvested Syrah grape

Irrigation Amount	Irrigation Frequency	Juice pH			TSS (Brix)			Berry Weight (g/berry)		
		2014	2015	2016	2014	2015	2016	2014	2015	2016
70/35	1×	3.55	3.42	3.52	28.1	25.6 ab	24.1	1.13	1.25 ab	1.27
	3×	3.37	3.80	3.54	28.1	27.5 a	24.5	1.18	1.35 a	1.25
70/70	1×	3.25	3.27	3.64	27.9	23.8 b	26.1	1.26	1.06 b	1.46
	3×	3.27	3.27	3.66	27.0	24.8 ab	22.8	1.21	1.17 ab	1.23
35/70	1×	3.35	3.54	3.65	28.8	25.5 ab	25.7	1.05	1.13 ab	1.28
	3×	3.23	3.14	3.55	27.0	24.5 ab	25.2	1.09	1.13 ab	1.23
35/35	1×	3.42	3.51	3.69	26.4	26.7 a	24.1	1.08	1.09 b	1.33
	3×	3.33	3.58	3.35	27.8	26.6 a	22.5	1.21	1.22 ab	1.26

Mean values for juice pH, TSS and berry weight. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n=3$ independent field samples). ns, not significant.

Table 2.3a Composition of volatile compounds in Malbec grapes with vineyard water management from 2014 to 2016 (ug/kg)

Compound	Mean values ^a					<i>p-values</i> ^b				
	Year			Irrigation frequency		Year	Year × Irrigation Amount	Irrigation Amount	Irrigation Frequency	Irrigation Amount × Frequency
	2014	2015	2016	1×	3×					
<i>C₆ Compounds</i>										
Hexanal	2490 b	2165 b	3833 a	2503	2478	<0.001	ns	ns	ns	ns
E-2-Hexenal	1445b	687 c	10764 a	4421	4315	<0.001	0.002	0.021	ns	ns
Hexanol	1148 a	531 c	927 b	817	927	<0.001	ns	ns	ns	ns
<i>Terpenes</i>										
Linalool oxide	0 c	1.79 a	0.27 b	0.71	0.75	<0.001	ns	ns	ns	ns
Linalool	0 c	1.87 a	0.29 b	1	1.13	<0.001	ns	ns	ns	ns
α-Terpineol	0.61 b	0.62 a	0.09 b	0.27	0.6	<0.001	ns	0.011	<0.001	ns
β-Citronellol	0 b	0.05 b	0.31 a	0.11	0.13	0.004	ns	ns	ns	ns
Geraniol	6.86 b	13.4 a	7.23 b	9.94	8.77	<0.001	0.013	0.003	ns	ns
Nerol	0 b	0.07 ab	0.13 a	0.05	0.09	0.015	ns	ns	ns	ns
<i>C₁₃-norisoprenoids</i>										
trans-β-damascenone	12.8 b	8.7 c	15.3 a	12.5	11.9	<0.001	0.014	ns	ns	ns
β-ionone	0.26 b	0.19 b	0.61 a	0.35	0.37	<0.001	ns	ns	ns	ns
Vitispirane ^c	16.4 a	14.2 b	1.80 c	10.9	10.4	<0.001	ns	ns	ns	ns
TDN ^c	16.5 b	28.2 a	7.90 c	17.4	18	<0.001	ns	ns	ns	ns
<i>Miscellaneous</i>										
1-Octanol	2.08 b	0.24 c	4.41 a	2.2	2.17	<0.001	0.015	0.001	ns	ns
1-Octen-3-ol	5.56 b	10.02 a	11.2 a	8.07	9.41	0.002	0.01	ns	ns	ns
Benzyl Alcohol	132 a	72.4 b	117.9 a	95.1	116	<0.001	0.017	<0.001	0.004	ns
Phenylethyl alcohol	55.0 b	27.7 c	86.1 a	58.1	52.8	<0.001	0.003	0.001	ns	ns
Hexanoic Acid	561 b	276 c	666 a	447	541	<0.001	ns	<0.001	0.043	ns

^a Means with different letters between year or irrigation frequency columns within a row differ significantly at $p \leq 0.05$ by Tukey HSD t test. ns indicates not significant

^b Results from a mixed model analysis of variance with year, irrigation amount, Irrigation frequency and their interactions as fixed effects.

^c:vitispirane and TDN estimated on the basis of β-damascenone

Table 2.3b Composition of volatile compounds in Malbec grapes with different vineyard water management treatments from 2014 to 2016 (ug/kg)

Year ^a	Irrigation mount	C ₆ compounds	Terpenes		C ₁₃ -norisoprenoids			Miscellaneous		
		E-2-Hexenal	α -Terpineol	Geraniol	Trans- β -damascenone	1-Octanol	1-Octen-3-ol	Benzyl alcohol	Phenylethyl alcohol	Hexanoic acid
2014	70/35	2683 a	0.99	6.10	12.0	2.20 ab	6.56 a	148	40.9 b	642 a
	70/70	2079 a	0.60	7.43	12.8	1.84 b	2.85 b	99	54.2 ab	427 b
	35/70	2535 ab	0.49	5.30	12.5	2.03 ab	5.31 ab	99	46.2 b	543 ab
	35/35	2665 a	0.27	8.03	13.8	2.26 a	7.54 a	181	73.6 a	659 a
2015	70/35	1380 b	0.79	13.8 ab	9.5 ab	0.51	11.8	105	41.1 a	289
	70/70	1333 b	0.40	18.9 a	10.1 a	0.13	8.49	61.3	27.2 ab	316
	35/70	1878 b	0.55	8.01 b	8.9 ab	0.13	11.8	42.5	17.0 b	139
	35/35	3936 a	0.61	13.8 ab	6.4 b	0.18	7.40	74.8	29.6 ab	338
2016	70/35	4081	1.05 a	10.56	17.9 a	5.28 a	9.02 b	114 ab	78	646 ab
	70/70	3696	0.31 b	6.16	14.8 ab	3.85 ab	7.52 b	100 b	81	578 b
	35/70	3459	0.33 b	5.98	14.7 b	3.44 b	7.65 b	105 b	82	565 b
	35/35	4095	0.20 b	10.38	13.7 b	5.08 a	20.71 a	152 a	102	963 a

a. Mean values followed by different letters differ significantly at $p \leq 0.05$ by Tukey HSD t test.

Table 2.4a Composition of volatile compounds in Syrah grapes with different vineyard water management treatment from 2014 to 2016 (ug/kg)

Compound	Mean values ^a					<i>p-values</i> ^b				
	Year			Irrigation frequency		Year	Year × Irrigation Amount	Irrigation Amount	Irrigation Frequency	Irrigation Amount × Frequency
	2014	2015	2016	1×	3×					
<i>C₆ Compounds</i>										
Hexanal	3504 a	1018	3705 a	2821	2664	<0.001	ns	ns	ns	ns
E-2-Hexenal	2181 b	296 c	19860 a	7185	7706	<0.001	ns	ns	ns	ns
Hexanol	781 b	1161 a	1441 a	1126	1129	<0.001	ns	ns	ns	ns
<i>Terpenes</i>										
Linalool oxide	0.03 c	1.79 a	0.4 b	0.77	0.71	<0.001	ns	ns	ns	ns
Linalool	0.34 b	1.98 a	0.64 b	0.89	1.08	<0.001	0.023	ns	ns	ns
α-Terpineol	0 b	0.84 a	0.03 b	0.21 b	0.38 a	<0.001	ns	ns	0.037	ns
β-Citronellol	0 b	0.02 b	0.54 a	0.24 a	0.13 b	0.004	ns	ns	0.032	ns
Geraniol	2.02 b	9.1 a	9.99 a	7.41	6.66	<0.001	ns	ns	ns	ns
Nerol	0 c	0.07 b	0.57 a	0.26	0.17	0.015	0.005	0.025	0.009	ns
<i>C₁₃-norisoprenoids</i>										
trans-β-damascenone	9.21 b	5.61 c	11.6 a	8.2	9.4	<0.001	ns	ns	ns	ns
β-ionone	0.74 a	0.25 b	0.8 a	0.59	0.61	<0.001	ns	ns	ns	ns
Vitispirane ^c	17.5 b	28.0 a	13.9 c	17.8 b	21.8 a	<0.001	0.001	<0.001	<0.001	ns
TDN ^c	16.5 b	52.8 a	14.9 b	25.5 b	30.6 a	<0.001	<0.001	<0.001	0.003	ns
<i>Miscellaneous</i>										
1-Octanol	1.71 b	0.31 c	5.48 a	2.56	2.44	<0.001	0.029	0.006	ns	ns
1-Octen-3-ol	10 ab	7.19 b	11.8 a	9.37	9.95	0.002	ns	0.016	ns	ns
Benzyl Alcohol	99.9 b	148 a	140 a	135	124	0.005	ns	ns	ns	ns
Phenylethyl alcohol	97.1 a	34.3 b	91.2 a	85.4 a	63 b	<0.001	ns	ns	0.001	ns
Hexanoic Acid	326 b	325 b	639 a	482 a	379 b	<0.001	0.001	0.027	0.001	ns

a Means with different letters between year or irrigation frequency columns within a row differ significantly at $p \leq 0.05$ by Tukey HSD t test. ns indicates not significant

b Results from a mixed model analysis of variance with year, irrigation amount, Irrigation frequency and their interactions as fixed effects.

c: vitispirane and TDN estimated on the basis of β-damascenone

Table 2.4b Composition of volatile compounds in Syrah grapes with vineyard water management from 2014 to 2016 (ug/kg)

Year ^a	Irrigation amount	Terpenes		C ₁₃ -norisoprenoids		Miscellaneous		
		Linalool	Nerol	Vitispirane	TDN	1-Octanol	1-Octen-3-ol	Hexanoic acid
2014	70/35	0	0	17.3	16.4	2.05	8.44	319
	70/70	0	0	17.3	16.4	1.7	9.21	314
	35/70	0	0	17.5	16.5	1.57	10.7	339
	35/35	0	0	17.9	16.7	1.53	11.8	331
2015	70/35	1.47	0.04 b	23.8 b	47.6 b	0.25	5.58	299
	70/70	2.11	0.08 ab	22.9 b	43.1 b	0.43	8.19	377
	35/70	2.89	0.11 a	28.6 ab	50.9 b	0.33	9.06	272
	35/35	1.43	0.06 ab	36.7 a	69.5 a	0.23	5.9	354
2016	70/35	0.63 ab	0.76 a	10	15	6.45 a	9.33 b	513 b
	70/70	0.69 ab	0.56 ab	16.5	15.9	4.95 b	9.56 b	514 b
	35/70	0.85 a	0.65 ab	12.6	10.5	5.5 ab	16.7 a	884 ab
	35/35	0.37 b	0.33 b	16.6	18.1	5.01 b	11.5 ab	644 ab

a. Mean values followed by different letters differ significantly at $p \leq 0.05$ by Tukey HSD t test.

Table 2.5 C₁₃-norisoprenoids in Malbec grapes harvested in 2014, 2015 and 2016 subjected to different deficit irrigation timing

Compounds	<i>Mean value ± SD</i> ^a			<i>p-value</i> ^b					
	2014	2015	2016	Year	Year × EBV	Year × EAV	EBV	EAV	EAV×EBV
Trans-β-damascenone	12.8±1.1	8.70±2.36	15.3±2.6	<0.001	0.008	0.017	0.008	ns	ns
β-ionone	0.26±0.08	0.19±0.07	0.62±0.21	<0.001	ns	ns	ns	ns	ns
Vitispirane ^c	16.4±0.25	14.3±1.5	1.8±0.7	<0.001	ns	ns	ns	ns	ns
TDN ^c	16.5±0.5	28.2±5.1	7.9±4.1	<0.001	ns	ns	ns	ns	ns

a Means ± SD presented. ns indicates not significant

b Results from a mixed model analysis of variance with year, irrigation amount, Irrigation frequency and their interactions as fixed effects.

c: vitispirane and TDN estimated on the basis of β-damascenone

EBV: ETc variation before veraison EAV: ETc variation After veraison

Table 2.6 C₁₃-norisoprenoids in Syrah grapes harvested in 2014, 2015 and 2016 subjected to different deficit irrigation timing

Compounds	<i>Mean value ± SD</i> ^a			<i>p-value</i> ^b					
	2014	2015	2016	Year	Year × EBV	Year × EAV	EBV	EAV	EAV×EBV
Trans-β-damascenone	9.2±0.6	5.6±2.3	11.6±4.9	<0.001	ns	ns	ns	ns	ns
β-ionone	0.74±0.13	0.25±0.11	0.80±0.32	<0.001	ns	ns	ns	ns	ns
Vitispirane ^c	17.5±0.67	28.0±7.6	13.9±7.2	<0.001	0.007	ns	0.004	0.017	ns
TDN ^c	16.5±0.3	52.8±14.0	14.9±9.4	<0.001	0.002	ns	0.018	0.052	0.011

a Means ± SD presented. ns indicates not significant

b Results from a mixed model analysis of variance with year, irrigation amount, Irrigation frequency and their interactions as fixed effects.

c: vitispirane and TDN estimated on the basis of β-damascenone

EBV: ETc variation before veraison EAV: ETc variation After veraison

Table 2.7a Free C₁₃-norisoprenoids in Malbec grapes with different irrigation treatments (μg/L)

Irrigation Amount	Irrigation Frequency	trans-β-damascenone			β-ionone		
		2014	2015	2016	2014	2015	2016
70/35	1×	0.41	1.75	0.35	nd	0.03	nd
	3×	0.40	1.84	0.20	nd	0.08	nd
70/70	1×	nd	1.56	0.33	nd	0.02	nd
	3×	0.30	2.16	0.29	nd	0.04	nd
35/70	1×	0.52	1.13	0.12	nd	0.13	nd
	3×	0.55	1.89	0.20	nd	0.12	nd
35/35	1×	0.50	1.15	0.69	nd	0.14	nd
	3×	0.50	1.89	0.19	nd	0.12	nd

Mean values presented. nd: not detected

Table 2.7b Free C₁₃-norisoprenoids in Syrah grapes with different irrigation treatments (µg/L)

Irrigation Amount	Irrigation Frequency	trans-β-damascenone			β-ionone		
		2014	2015	2016	2014	2015	2016
70/35	1×	0.45	0.23	0.13	nd	0.05	0.03
	3×	0.43	0.37	0.19	nd	0.07	0.09
70/70	1×	0.22	0.26	0.21	nd	0.06	0.04
	3×	0.35	0.50	0.25	nd	0.06	0.09
35/70	1×	0.37	0.30	0.67	nd	0.08	0.02
	3×	0.83	0.23	0.19	nd	0.04	0.02
35/35	1×	2.07	0.27	0.55	nd	0.10	0.02
	3×	0.43	0.37	0.19	nd	0.10	0.04

Mean values presented. nd: not detected

Table 2.8a. Concentration of major volatiles with different irrigation treatments (ug/kg) in 2016 Malbec grape berries

Irrigation Amount Irrigation Frequency	70/35		70/70		35/70		35/35		<i>p</i> -value
	1×	3×	1×	3×	1×	3×	1×	3×	
<i>C₆ Compounds</i>									
Hexanal	3770±1302	4392±1327	3612±763	3779±1238	3675±1387	3243±810	4819±2246	3370±1206	ns
E-2-Hexenal	12054±1264 a	12005±1491 a	12066±366 a	11122±769 ab	9296±1907 ab	7983±423 b	12210±3497 a	9378±1433 ab	0.038
Hexanol	874±411	1139±422	767±92	793±295	799±360	876±150	1265±428	898±278	ns
<i>Terpenes</i>									
Linalool oxide	0.12±0.16	0.15±0.12	0.31±0.49	0.06±0.05	0.19±0.14	0.49±0.17	0.44±0.53	0.67±0.88	ns
Linalool	0.22±0.25	0.6±0.18	0.4±0.58	0.04±0.01	0.81±0.45	0.06±0.04	0.11±0.07	0.7±0.35	ns
α-Terpineol	0.21±0.11 b	0.04±0.06 b	3.79±0.14 a	4.76±1.86 a	3.69±0.03 a	3.67±0 a	3.75±0.05 a	3.89±0.32 a	<0.001
β-Citronellol	0.82±0.66	0.48±0.72	0.06±0.04	0.34±0.52	0.2±0.29	0.04±0.01	0.03±0.01	0.42±0.62	ns
Geraniol	7.1±2.63 bc	14±8 ab	6.83±1.54 bc	5.48±0.28 bc	5.05±0.91 c	6.9±0.38 bc	12.3±3.87 ab	8.45±2.04 bc	0.048
Nerol	0.02±0.01	0.78±0.7	0.01±0	0.08±0.12	0.01±0	0.01±0.01	0.46±0.75	0.02±0.02	ns
<i>C₁₃-norisoprenoids</i>									
trans-β-damascenone	18.7±4.2	17.1±2.1	14.2±1.8	15.5±3.1	15.4±0.8	14±2.6	13.6±0.5	13.8±1.2	ns
β-ionone	0.52±0.08	0.88±0.3	0.69±0.28	0.45±0.13	0.5±0.03	0.52±0.15	0.66±0.22	0.67±0.16	ns
Vitispirane	2.48±1.01	2.32±1.07	1.37±0.1	2.08±0.9	1.47±0.06	1.18±0.46	1.77±0.46	2.05±0.58	ns
TDN	12.4±5.7	7.5±3.3	4.6±0.7	9.8±3.3	6±1.1	6.4±4.5	7±2.6	9.2±6.4	ns
<i>Miscellaneous</i>									
1-Octanol	5.32±1.14	5.24±0.52	4.02±0.07	3.69±0.42	3.56±0.44	3.33±0.56	5.62±2.06	4.53±0.94	ns
1-Octen-3-ol	14±4.32 ab	7.48±4.92 b	8.1±2.22 b	6.94±2.46 b	8.02±6.89 b	7.29±3.8 b	21.35±7.43 a	20.08±8.54 a	0.036
Benzyl Alcohol	131.2±27.3	96.5±23	103±12	97±14.3	96.6±9.2	114±7	169±68	136±16	ns
Phenylethyl alcohol	94.9±14.3	60.6±28.5	82.8±6	79.9±5.9	77.8±6.6	86.9±3.9	111.9±36.4	92.9±11.8	ns
Hexanoic Acid	625±218 b	667±212 b	637±138 b	520±36 b	472±97 b	658±30 b	1134±342 a	792±181 b	0.010

Means ± SD presented. Different letters represent significantly (Tukey HSD, P<0.05) different in means (n=3 independent field samples). ns, not significant. vitispirane and TDN estimated on the basis of β-damascenone

Table 2.8b. Concentration of major volatiles (ug/kg) with different irrigation treatments in 2015 Malbec grape berries

Irrigation Amount	70/35		70/70		35/70		35/35		p-value
	1×	3×	1×	3×	1×	3×	1×	3×	
<i>C₆ Compounds</i>									
Hexanal	2223±635 ab	818±449 b	1496±367 b	1567±324 ab	1392±462 b	1353±189 ab	4304±135 a	3568±1142 ab	0.007
E-2-Hexenal	627±135	587±84	578±286	715±12	660±327	740±110	785±40	803±231	ns
Hexanol	505±312	914±311	277±107	516±167	445±317	477±125	460±142	655±246	ns
<i>Terpenes</i>									
Linalool oxide	1.78±0	1.8±0.02	1.79±0.01	1.79±0.01	1.8±0.02	1.78±0	1.78±0	1.8±0.03	ns
Linalool	2.45±0.7	2.07±1.18	2.2±1.44	2.5±0.13	1.39±0.81	1.94±0.88	0.84±0.28	1.58±1.89	ns
α-Terpineol	0.75±0.21	0.83±0.35	0.42±0.29	0.73±0.64	0.49±0.19	0.53±0.34	0.33±0.27	0.88±0.65	ns
β-Citronellol	0.06±0.01	0.06±0	0.06±0.03	0.08±0.11	0.03±0.03	0.02±0.04	0.02±0.04	0.06±0	ns
Geraniol	16.2±4.35	8.01±6.17	18.9±7.8	21.6±5.22	9.56±2.74	5.57±5.11	14.5±5.33	13.2±8.8	ns
Nerol	0.05±0.01	0.06±0	0.04±0.02	0.1±0.06	0.03±0.03	0.04±0.03	0.06±0.07	0.09±0.04	ns
<i>C₁₃-norisoprenoids</i>									
trans-β-damascenone	10.4±1.8	8.6±0.7	10.2±1.9	10±0.6	9.6±0.9	8.2±2.4	7.1±2.4	5.7±3.8	ns
β-ionone	0.22±0.09	0.21±0.08	0.26±0.09	0.17±0.04	0.12±0.06	0.22±0.04	0.15±0.08	0.18±0.04	ns
Vitispirane	14.1±2.4	13.5±0.3	14.6±2.5	14.4±2.2	13.8±0.2	13.4±1	15.9±0.8	14.1±1.1	ns
TDN	27±4.2	36±3.3	30.3±6.9	27.2±1.6	27.2±5	26.2±2.7	24.4±7	27.3±2.5	ns
<i>Miscellaneous</i>									
1-Octanol	0.79±0.58a	0.24±0.12ab	0.16±0.06b	0.09±0.01b	0.11±0.02b	0.14±0.07b	0.22±0.09ab	0.14±0b	0.002
1-Octen-3-ol	11.6±5.98	12±7.99	8.58±7.36	8.38±2.05	9.57±3.88	15.2±2.42	4.9±2.4	9.91±7.72	ns
Benzyl Alcohol	100±35.3	109±22.4	46.9±34.9	75.6±15.5	51.3±31	46.6±37.7	59.5±13.7	90.2±26.7	ns
Phenylethyl alcohol	33.9±13.5	48.3±19.9	32.3±17.9	22.1±5.82	20.4±1.29	15.3±6.11	31.6±16.1	17.6±19	ns
Hexanoic Acid	165±75bc	414±204ab	198±115abc	434±158a	72±54c	244±54abc	315±164abc	361±141ab	0.04

Means ± SD presented. Different letters represent significantly (Tukey HSD, P<0.05) different in means (n=3 independent field samples). ns, not significant. vitispirane and TDN estimated on the basis of β-damascenone

Table 2.8c. Concentration of major volatiles (ug/kg) with different irrigation treatments in 2014 Malbec grape berries

Irrigation Amount	70/35		70/70		35/70		35/35		<i>p</i> -value
	1×	3×	1×	3×	1×	3×	1×	3×	
<i>C</i>₆ Compounds									
Hexanal	2855±112 a	2510±37 abc	1998±41 c	2159±302 bc	2299±331 c	2771±256 ab	2781±176 ab	2550±178 abc	<0.001
E-2-Hexenal	1542±151	1906±919	949±99	1089±162	1131±198	1983±854	1473±102	1490±145	ns
Hexanol	949±124	1318±103	1286±331	1089±394	860±139	1079±185	1337±435	1261±394	ns
<i>Terpenes</i>									
α-Terpineol	0.97±0.49 ab	1±0.53 ab	0±0 b	1.51±0.02 ab	0±0 b	0.99±0.35 ab	0±0 b	0.68±0.32 ab	0.001
Geraniol	5.49±1.14	6.7±1.28	6.49±1.47	8.84±2.19	5.2±1.58	5.37±1.14	8.47±4.55	7.58±1.98	ns
<i>C</i>₁₃-norisoprenoids									
trans-β-damascenone	11.6±0.4	12.4±0.7	12.5±0.7	13.1±0.8	12.4±1.3	12.7±0.2	14.4±1.7	13.1±0.5	ns
β-ionone	0.18±0.01 c	0.22±0.02 bc	0.24±0.08 bc	0.31±0.06 ab	0.22±0.06 abc	0.21±0.01 bc	0.39±0.04 a	0.31±0.03 ab	0.001
Vitispirane	16.4±0.2	16.4±0.2	16.4±0.1	16.6±0.3	16.3±0.1	16.2±0.1	16.8±0.2	16.5±0.3	ns
TDN	16.4±0.2	16.3±0.1	16.3±0.2	16.3±0.1	16.3±0.1	16.3±0	17.4±0.9	16.9±0.4	ns
<i>Miscellaneous</i>									
1-Octanol	2.15±0.26	2.24±0.13	1.86±0.14	1.82±0.29	1.96±0.3	2.1±0.17	2.19±0.21	2.33±0.11	ns
1-Octen-3-ol	7.42±1.88 ab	5.69±2.71 b	2.49±0.32 b	3.22±0.58 b	4.93±1.17 ab	5.69±1.18 ab	6.27±0.16 ab	8.81±0.76 a	0.009
Benzyl Alcohol	135±47 b	161±86 ab	79±24 b	119±41 b	96±21 b	102±10 b	105±18 b	257±68 a	0.003
Phenylethyl alcohol	45.2±1.3 ab	36.5±1.6 b	53±2.1 ab	55.5±8 ab	46.7±7.3 ab	45.2±10.1 ab	68.1±25.7 ab	79.2±6 a	0.022
Hexanoic Acid	640±109 abc	643±87 ab	399±81 c	454±110 bc	496±51 abc	591±43 abc	576±35 abc	742±15 a	0.008

Means ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n=3$ independent field samples). ns, not significant. vitispirane and TDN estimated on the basis of β-damascenone

Table 2.9a. Concentration of major volatiles (ug/kg) with different irrigation treatments in 2016 Syrah grape berries

Irrigation Amount Irrigation Frequency	70/35		70/70		35/70		35/35		<i>p</i> -value
	1×	3×	1×	3×	1×	3×	1×	3×	
<i>C₆ Compounds</i>									
Hexanal	3561±702 ab	3562±245 ab	3871±773 ab	3662±546 ab	3164±333 b	3753±302 ab	4799±720 a	3271±436 ab	0.058
E-2-Hexenal	17419±2107	19086±2987	16419±6135	19929±2175	15888±1575	25095±7918	25880±1211	19165±1222	ns
Hexanol	1285±420	1142±337	1556±678	1305±682	1641±431	1799±427	1414±588	1383±424	ns
<i>Terpenes</i>									
Linalool oxide	0.45±0.65	0.25±0.18	0.19±0.09	0.35±0.5	0.22±0.03	0.15±0.11	0.25±0.1	0.31±0.17	ns
Linalool	0.56±0.09 ab	0.7±0.18 ab	0.93±0.25 a	0.45±0.07 ab	0.84±0.2 a	0.87±0.25 a	0.44±0.12 b	0.45±0.01 ab	0.006
α-Terpineol	0.01±0.01	0.03±0.04	0.03±0.02	0.01±0	0.03±0.02	0.02±0.01	0.06±0.08	0.01±0.01	ns
β-Citronellol	0.63±0.43	0.85±0.05	1.07±0.14	0.17±0	0.61±0.36	0.66±0.2	0.5±0.08	0.65±0.15	ns
Geraniol	10.8±1.3 ab	11.1±1.8 a	12.3±1.7 a	7.54±1.59 b	11.7±2.3 a	9.49±0.93 ab	9.69±2.74 ab	7.32±1.43 b	0.033
Nerol	0.88±0.17 a	0.64±0.09 abc	0.74±0.06 ab	0.38±0.11 bc	0.8±0.02 ab	0.74±0.06 abc	0.62±0.25 bc	0.24±0.16 c	0.037
<i>C₁₃-norisoprenoids</i>									
trans-β-damascenone	10.9±4.2	14.7±7.1	7.6±4.1	16±1.7	6.6±1.6	12.3±5.5	9.9±4.6	14.5±3.5	ns
β-ionone	0.79±0.14	1.14±0.54	0.8±0.28	0.85±0.12	0.46±0.05	0.97±0.38	0.64±0.2	0.78±0.36	ns
Vitispirane	7.7±2.1 b	12.4±3.4 b	9.5±4.0 b	23.5±4.7 a	9.3±3.4 b	15.9±5.1 ab	10.0±4.4 b	23.3±7.5 a	0.002
TDN	13.6±10 abc	16.5±5.7 abc	5.8±2.9 c	26±8.2 ab	8.5±4.2 bc	12.5±4.1 abc	8.3±4 bc	27.9±8 a	0.004
<i>Miscellaneous</i>									
1-Octanol	6.07±0.42 ab	6.82±0.29 a	5.32±0.91 ab	4.61±0.27 b	5.68±0.62 ab	5.33±0.29 ab	5.71±1.76 ab	4.31±0.39 b	0.028
1-Octen-3-ol	6.9±0.9 b	11.7±4.3 ab	11.8±4.9 ab	7.3±1 b	18.5±7.7 a	15±0.7 ab	11.5±2.8 ab	11.4±0.9 ab	0.032
Benzyl Alcohol	153±51	134±5	174±34	90±30	146±39	107±15	112±43	95±26	ns
Phenylethyl alcohol	101±20	85.7±3.3	135.7±8.9	56.2±9.1	101±24	69.9±6.3	71.3±27.6	56.4±14.6	ns
Hexanoic Acid	557±33 bc	469±53 bc	688±219 bc	341±7 c	1066±149 a	702±300 b	773±320 ab	515±55 bc	0.007

Means ± SD presented. Different letters represent significantly (Tukey HSD, P<0.05) different in means (n=3 independent field samples). ns, not significant.

vitispirane and TDN estimated on the basis of β-damascenone

Table 2.9b. Concentration of major volatiles (ug/kg) in 2015 Syrah grape berries

Irrigation Amount	70/35		70/70		35/70		35/35		<i>p</i> -value
	1×	3×	1×	3×	1×	3×	1×	3×	
<i>C₆ Compounds</i>									
Hexanal	1241±306	1043±184	1157±603	1008±599	1345±673	693±308	557±72	1100±316	ns
E-2-Hexenal	897±71	620±131	895±76	725±173	698±97	737±276	746±234	722±129	ns
Hexanol	1063±139	1372±866	1429±759	1355±235	1041±149	1346±534	1351±386	1102±268	ns
<i>Terpenes</i>									
linalool oxide	1.78±0	1.8±0.02	1.78±0	1.82±0.05	1.79±0.02	1.78±0	1.78±0	1.78±0	ns
linalool	0.89±0.3	2.04±1.16	1.68±0.87	2.54±2.35	1.77±0.53	4.01±2.82	0.98±0.69	1.89±0.12	ns
alpha-terpineol	0.49±0.02	0.73±0.37	0.62±0.2	1.07±0.98	0.74±0.37	1.79±0.81	0.46±0.38	0.83±0.73	ns
geraniol	9.47±1.45	10.96±1.73	7.55±0.86	6.33±4.2	12.87±4.24	7.76±5.88	7.48±6.17	10.4±6.53	ns
nerol	0.03±0.03	0.05±0.04	0.07±0.01	0.1±0.03	0.13±0.08	0.1±0.04	0.07±0	0.06±0.05	ns
<i>C₁₃-norisoprenoids</i>									
trans-β-damascenone	6.84±2.48	3.72±1.43	6.76±2.97	5.01±1.95	4.9±3.7	4.5±2.63	7.41±0.82	5.73±0.88	ns
β-ionone	0.28±0.01 b	0.22±0.07 b	0.17±0.06 b	0.19±0.03 b	0.26±0.04 b	0.14±0.04 b	0.48±0.08 a	0.24±0.14 b	0.001
Vitispirane	25±5.5 b	22.6±7.1 b	24.4±5.1 b	21.3±3.7 b	25.8±7.1 ab	31.4±3.3 ab	32.9±5.6 ab	40.5±4.2 a	0.007
TDN	51±2.1 ab	44.2±16.6 b	44.2±11.3 b	42±8.7 b	46±10.3 b	55.8±3.1 ab	62.6±7.1 ab	76.5±11.6 a	0.008
<i>Miscellaneous</i>									
1-Octanol	0.17±0.05	0.33±0.14	0.18±0.09	0.69±0.55	0.29±0.24	0.37±0.21	0.23±0.14	0.23±0.08	ns
1-Octen-3-ol	5.07±1.62	6.1±3.5	6.08±2.97	10.31±7.94	9.32±7.58	8.8±4.48	3.46±1.4	8.35±4.82	ns
Benzyl Alcohol	125.5±8.5	167.5±40.4	78.5±34.5	205±70.4	160.9±3.1	140.7±48.4	135.6±69.1	171.3±52.7	ns
Phenylethyl alcohol	19±0	42±29.4	20.1±1.4	25.9±18.5	34.1±21.3	34.3±29.2	56.1±37.7	43.2±16.6	ns
Hexanoic Acid	297±56	301±118	487±107	267±87	263±43	280±86	339±140	368±83	ns

Means ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n=3$ independent field samples). ns, not significant. vitispirane and TDN estimated on the basis of β-damascenone

Table 2.9c. Concentration of major volatiles (ug/kg) in 2014 Syrah grape berries

Irrigation Amount	70/35		70/70		35/70		35/35		<i>p-value</i>
	1×	3×	1×	3×	1×	3×	1×	3×	
<i>C₆ Compounds</i>									
Hexanal	3866±323	3673±90	3202±66	3223±725	3468±397	3272±600	3623±304	3705±362	ns
E-2-Hexenal	2327±218	1952±230	2124±274	1895±213	2343±525	2044±581	2554±231	2208±180	ns
Hexanol	713±56 b	727±8 b	739±85 b	718±100 b	674±230 b	852±82 ab	983±40 a	844±119 ab	<0.001
<i>C₁₃-norisoprenoids</i>									
trans-β-damascenone	9.21±0.74	9.16±1.31	9.26±0.04	8.96±0.35	9.45±0.77	8.94±0.59	9.56±0.64	9.16±0.33	ns
β-ionone	0.88±0.18	0.77±0.09	0.68±0.05	0.7±0.01	0.86±0.19	0.69±0.11	0.77±0.12	0.62±0.05	ns
Vitispirane	17.2±0.2	17.5±1.2	17.1±0.6	17.6±0.3	17.7±0.9	17.3±0.2	17.7±0.8	18.1±0.9	ns
TDN	16.3±0.1	16.4±0.5	16.2±0	16.5±0.1	16.7±0.5	16.3±0.1	16.5±0.3	16.8±0.5	ns
<i>Miscellaneous</i>									
1-Octanol	2.38±0.86 a	1.73±0.13 a	1.97±0.44 a	1.43±0.19 ab	2.06±0.5 a	1.07±0.93 ab	0.7±0.46 b	2.36±0.44 a	0.021
1-Octen-3-ol	10.55±2.53	6.33±0.53	10.25±1.38	8.14±0.82	9.69±3.53	11.64±5.24	9.35±0.93	14.31±5.85	ns
Benzyl Alcohol	144±10 a	97±18 ab	96±21 ab	92±23 ab	98±30 ab	98±22 ab	88±5 ab	85±13 b	<0.001
Phenylethyl alcohol	140±3	83±14	105±21	92±23	94±23	84±32	95±38	85±21	ns
Hexanoic Acid	317±15	321±8	290±4	339±67	376±84	302±7	336±18	323±18	ns

Means ± SD presented. Different letters represent significantly (Tukey HSD, P<0.05) different in means (n=3 independent field samples). ns, not significant. vitispirane and TDN estimated on the basis of β-damascenone

Table 2.10 YAN concentration in Malbec grape must of 2014, 2015 and 2016

Irrigation Amount	Irrigation Frequency	YAN (mg/L)		
		2014	2015	2016
70/35	1×	195 ± 56	232±18	186±15 abc
	3×	172 ± 18	196±28	234±48 ac
70/70	1×	191 ± 18	206±52	170±19 bc
	3×	180 ± 49	179±32	114±42 c
35/70	1×	177 ± 15	236±31	207±22 abc
	3×	157 ± 18	314±62	278±74 ab
35/35	1×	199 ± 66	213±45	290±46 a
	3×	155 ± 20	199±17	293±18 a

Means ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n = 3$ independent field samples).

Table 2.11 YAN concentration in Malbec grape must of 2014, 2015 and 2016

Irrigation Amount	Irrigation Frequency	YAN (mg/L)		
		2014	2015	2016
70/35	1×	228 ± 17	218±36 abc	149±13 ab
	3×	211 ± 7	240±58 abc	122±19 ab
70/70	1×	198 ± 71	201±16 bc	137±10 ab
	3×	183 ± 21	178±41c	88±15 b
35/70	1×	191 ± 74	230±15 abc	188±32 a
	3×	183 ± 20	255±3 abc	165±17 a
35/35	1×	209 ± 82	302±44 ab	139±13 ab
	3×	217 ± 49	286±9 a	157±33 a

Mean ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n = 3$ independent field sample)

Table 2.12a Weather data of vineyard for 2014, 2015 and 2016 seasons

	2014	2015	2016	1994–2012 average
Precipitation (mm)	88	113	120	99.6 ± 35
Daily average total direct solar radiation (MJ m ⁻²)	22.3	21.9	22.6	22.1 ± 0.9
Days daily maximum temperature exceeded 35°C	27	25	26	28 ± 12
^Z Accumulated growing degree days (°C)	1759	1865	1688	1708 ± 115
Alfalfa-based reference evapotranspiration (ET _r) (mm)	1314	1265	1329	1212 ± 55

^ZAccumulated growing degree days were calculated from daily maximum and minimum temperature with no upper limit and a base temperature of 10°C.

Table 2.12b Mean daily temperature of vineyard for 2014, 2015 and 2016 seasons (°F)

	2014	2015	2016
January	26.1	28.1	23.2
February	32.3	36.4	28.5
March	39.8	43.2	39.4
April	45.5	45.7	49.0
May	56.0	54.6	53.9
June	61.1	66.8	64.9
July	71.0	66.8	68.7
August	65.4	67.8	66.7
September	59.8	61.0	57.4

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**CHAPTER 3 FROM VINE TO WINE: EFFECT OF DEFICIT IRRIGATION ON
MALBEC AND SYRAH WINE QUALITY**

Xiaoxi Yuan, Yanping Qian, Michael C. Qian*

Department of Food Science and Technology, Oregon State University, Corvallis, OR
97331

*Corresponding author: Michael Qian. phone: 541-737-9114, fax: 541-737-1877, email:

Michael.Qian@oregonstate.edu

3.1 Abstract

This study investigated the impact of regulated deficit irrigation during grape berry development on Syrah and Malbec wine volatile composition. Four irrigation regimes [70 % ET_c from fruit set to veraison, 35 % ET_c from veraison to harvest (70/35), 70% ET_c sustained from fruit set to harvest (70/70), 35 % ET_c from fruit set to veraison, 70 % ET_c from veraison to harvest (35/70), and 35% ET_c sustained from fruit set to harvest (35/35)] were applied to the vines with two irrigation frequencies (1x= one event per week, 3x=same irrigation amount apportioned into three irrigation events per week). Wines were produced from corresponding grapes from the 2015 and 2016 growing seasons. Yeast assimilable nitrogen (YAN) of the must was measured as sum of primary amino nitrogen and ammonia nitrogen. Volatile compositions in wines were analyzed by SBSE-GC-MS, SPME-GC-MS, SPME-GC-FID and SPME-GC-PFPD technique. YAN concentration was affected by irrigation amount, among which 70/70 irrigation led to the lowest YAN concentration while the 35/35 treatment contributed to the highest YAN level in grape must before fermentation. Branch-chained esters and volatile phenolic compounds showed no significance among irrigation amounts in either Malbec or Syrah wines. For Malbec wines, β -damascenone in 2016 was high in 70% ET_c from fruit set to veraison treatments, but no difference was found in 2015. Irrigation amount showed no impact on C₁₃-norisoprenoids level in Syrah wines. Irrigation frequency in this study showed no impact on most of the volatiles in both Malbec and Syrah. Correlations were found between fermentation-derived volatile compounds and YAN level in grape must before fermentation. Isoamyl alcohol, isobutyl alcohol, Phenylethyl alcohol, ethyl phenyl acetate and phenyl ethyl acetate showed negative correlation with YAN concentration, while benzyl alcohol, ethyl butyrate, ethyl acetate and total straight chain esters increased with the increasing YAN level. The irrigation can alter the wine aroma profile by changing the YAN concentration in grape.

Key word: wine volatile composition, water stress, deficit irrigation, SPME, SBSE, YAN

3.2 Introduction

Environmental factors, including soil, topography, climate, and vineyard practice have been proven to influence grape and wine quality. Although the environment is dictated by site and climate of the vineyard, grape and wine quality can be enhanced by altering vineyard practice, such as irrigation, fertilization and pruning (D. Jackson and Lombard, 1993; R. S. Jackson, 2008). Water deficit is a common vineyard practice used in arid growing regions to enhance water use efficiency, limit canopy and berry growth and alter the biosynthesis of secondary metabolites associated with wine quality (Castellarin et al., 2007; Kennedy et al., 2002) Research has shown that vine water stress has its greatest impact on composition when water deficit occurs during the early phase of fruit development, prior to veraison (Cortell et al., 2005; M. Matthews et al., 1987; M. A. Matthews and Anderson, 1988). Drought conditions might lead to the poor shoot growth and fruit composition development, while excessive water may contribute a more vegetal and herbaceous aroma to wine (Chapman et al., 2005; M. Matthews et al., 1990; Myburgh, 2006). In general, moderate water deficit improves wine quality (Qian et al., 2009).

Aroma is one of the most important determinants for wine quality. The aroma compounds in wine are derived from multiple sources, including grapes, fermentation, storage and aging. Monoterpenes, norisoprenoids, phenylpropanoids, methoxypyrazines and volatile sulfur compounds in wine are grape-derived compounds, which can be manipulated by vineyard practice (González-Álvarez et al., 2013; Robinson et al., 2014). Higher alcohols, fatty acids and esters are generated through the yeast metabolism during fermentation (Bell and Henschke, 2005; Swiegers et al., 2005). Much research has demonstrated that reduced vine water availability through vineyard deficit irrigation could increase the levels of bound form terpenoids and C₁₃-norisoprenoids in grape berries, leading to final wines with less vegetative and more fruity aromas (Koundouras et al., 2009; Ou et al., 2010b; Qian et al., 2009; Song et al., 2012).

C₁₃-norisoprenoids are key odorants in wines, especially β -damascenone and β -ionone are important aroma compounds in wine due to their extremely low sensory threshold (Fang and Qian, 2005; Ferreira et al., 2000). C₁₃-norisoprenoids arise from carotenoid precursors found in grapes, and usually exist in bound forms in grapes until release by acid or enzymatic hydrolysis during wine making or aging (Williams et al., 1992). Researches have shown that vineyard practices, such as leaf removal (Feng et al., 2015; Lee and Skinkis, 2013), crop cover (Xi et al., 2011; Yuan et al., 2015) and irrigation (Bindon et al., 2007; Qian et al., 2009; Ristic et al., 2010) impact C₁₃-norisoprenoids. Deficit irrigation vines increased C₁₃-norisoprenoids in berries and corresponding wines (Qian et al., 2009). Bindon et al. (2007) pointed out that partial root zone drying (PRD) increased the hydrolytically released C₁₃-norisoprenoids in Cabernet Sauvignon.

Deficit irrigation during the growth period can alter the sensory profile of the wine (M. Matthews et al., 1990). In Cabernet Sauvignon, wine made from minimal irrigation showed stronger black berry, jam aroma compared with other irrigation treatments (Chapman et al., 2005). Wines made with Merlot grapes from 35% of estimated crop evapotranspiration produced more vitispirane, trans- β -damascenone, guaiacols than well-watered vines (Qian et al., 2009). Koundouras et al. (2006) reported that limited water supply improved the aroma and flavor of Agiorgitiko wines. Reynolds et al. (2007) reported that irrigated Chardonnay grapes had more intense apple, citrus and floral, but less earthy aromas compared to unirrigated ones. The objective of this study was to evaluate the effect of water stress on grape secondary metabolites and implication to Malbec and Syrah wine aroma compound profiles.

3.3 Methods

3.3.1 Chemicals

Standards of the non-isotope volatile compounds were purchased from commercial sources: Sigma-Aldrich (Milwaukee, WI), TCI America (Portland, OR), K & K Laboratories (Jamaica, NY), Alfa Aesar (Ward Hill, MA), Firmenich (Princeton, NJ),

and J & T Baker (Phillipsburg, NJ), with purity higher than 98% in all case. GC grade of methanol was obtained from EMD (Gibbstown, NJ) and ethanol was purchased from Aaper Alcohol and Chemical Co. (Shelbyville, KY). Tartaric acid was purchased from Mallinckrodt Inc. (Paris, KY).

Isotope compounds: ethyl butyrate-4,4,4-d₃ (99.8%), ethyl hexanoate-d₁₁ (98.7%), ethyl octanoate-d₁₅ (98.5%), hexanoic-d₁₁ acid (98.5%), decanoic-d₁₉ acid (98.6%), octanoic-d₁₅ acid (99.2%), (±)-linallol-d₃(vinyl-d₃) (99.2%), 2-phenyl-d₅-ethan-1,1,2,2-d₄-ol 98.5%), ethyl (±)-2-methylbutyrate-d₉ (99.1%) were purchased from CDN Isotopes Inc. (Canada). Ethyl decanoate-d₁₉ was synthesized by our lab.

3.3.2 Vineyard experimental design

The research was conducted over three consecutive growing seasons (2014-2017) in established field trials located at the University of Idaho Parma Research and Extension Center in Parma, ID (lat: 43°78'N; long: 116°94'W; 750 m asl). The soil (sandy loam, available water-holding capacity of 0.14 cm/cm soil), climatic conditions (semi-arid, dry steppe with warmest monthly average temperature of 32°C), and irrigation water supply (well water with sand media filter) at this location were well-suited for conducting deficit irrigation field research. The research was conducted in an irrigation trial that was planted in 2007 with the wine grape cultivars Malbec and Syrah. The vines in both trials were ungrafted (own-rooted), irrigated by above ground drip, and grown with the same training and trellis system (double-trunked, bilateral cordon, spur-pruned annually to 16 buds/m of cordon, vertical shoot positioned on a two-wire trellis with moveable wind wires). Vine water demand [Crop evapotranspiration (ET_c)] was estimated weekly using the 1982 Kimberly–Penman equation with alfalfa as a reference crop obtained from a local weather station (Agrimet) and a variable crop coefficient (0.3 to 0.7). Vineyard management reflected local commercial production practices including weed removal and periodic application of pesticides.

The 'Malbec' and 'Syrah' trials were located adjacent to one another and had the same vine by row spacing (1.8 x 2.4 m) and experimental design [split-plot with

irrigation amount (70 or 35% ETC sustained from fruit set to harvest, 35 increased to 70% at veraison, or 70 decreased to 35% at veraison) as the main factor and irrigation frequency (3 or 7d) as subplots]. Each plot contained 18 vines (three rows of six vines per row) with inner and outer rows considered borders. Replicate plots of each treatment level were plumbed together with independent flow meters and water supply control. Each trial perimeter contained two border vine rows under independent irrigation supply and control.

3.3.3 Wine making

Fruit was harvested from all plots. After harvest, grapes were transported to the lab in Corvallis, OR and stored at -24 °C overnight before being de-stemmed manually. One and a half kilograms of de-stemmed grapes were crushed. The must from each field replicates were fermented in the microscale fermentors (4 L) designed by Sampaio, Kennedy, and Vasconcelos (2007). 50 mg/L SO₂ was added to each ferment. Ferments were inoculated with Uvaferm 43 Dry Wine Yeast for Syrah wine and M Dry Wine Yeast for Malbec (Lalvin Bourgovin) and 0.3g/L Fermaid K were added to each fermentor. Fermentations were conducted in a temperature-controlled room at 26.6 °C. During fermentation, the punch-down disc was pushed halfway down so that the grapes were fully submerged. The sugar content (°Brix) was monitored using an Anton-Paar DMA 35N Density Meter (Graz, Austria). When all fermentations were complete, each sample was pressed twice using a presser that applied a constant pressure of 30 psi for 1 min for each pressing. Resulting wines were placed in a cold room at 4 °C to settle. Bottled wines were stored in the cold room at 4 °C before analysis.

3.3.4 Determination of wine Chemical composition

Total monomeric anthocyanin analysis

The spectrophotometric method based upon absorbance change under different pH (Giusti & Wrolstad, 2001) was used to assay total monomeric anthocyanins (TMA).

Before analysis, wine sample was diluted 5 times with milli-Q water. Each sample was assayed in duplicate. The concentration of monomeric anthocyanins (expressed as mg/L cyanidin-3-glucoside equivalent) was calculated based on the absorbance difference of two pH reaction solutions.

Total phenolic content analysis

Total Phenolic Content (TPC) was determined using the Folin–Ciocalteu colorimetric method (Singleton, 1988) with lower volumes. Standard curve was prepared the same day using solutions of gallic acid (40, 80, 120, 160 and 200 ppm). Assays were performed in triplicates, and values were reported as mg/L gallic acid equivalents.

3.3.5 Quantitative Analysis of Aroma Compounds

Major volatile Compounds.

Two mL of wine was diluted with 8 mL of saturated sodium chloride citric buffer (pH 3.5) in a SPME vial. Then 10 μ L of isotope internal standard mixture (ethyl octanoate-d15, 50 mg/L; ethyl butyrate-4,4,4-d3, 500 mg/L; ethyl(\pm)-2-methylbutyrate-d9, 200mg/L; 2-phenyl-d5-ethan-1,1,2,2-d4-ol, 1500 mg/L; ethyl decanoate-d19, 50 mg/L; (\pm)-linalol-d3(vinyl-d3), 100 mg/L; alpha-terpineol-d3, 200 mg/L; hexanoic-d11 acid, 1000 mg/L; octanoic-d15 acid, 500 mg/L; decanoic-d19 acid 200 mg/L) was added into the diluted sample. The volatiles in headspace were extracted by a preconditioned 2cm-50/30 μ m DVB/CAR/PDMS fiber (Supelco, Bellefonte, PA). The extraction and injection was conducted by autosampler (Gerstel, Linthicum, MD). Samples were first equilibrated at 50 °C in a thermostatic bath for 30 min and then extracted by SPME fiber for 30 min at the same temperature with stirring (500 rpm). After extraction, the fiber was inserted into the injection port of GC to desorb the analytes for 5 minutes. The injection was performed in the splitless mode and held at 250 °C. The analysis was performed on

an Agilent 6890 gas chromatograph equipped with an Agilent 5973 mass selective detector (Agilent Technologies, Santa Clara, CA). Compound separation was achieved using a ZB-WAX-PLUS column (30 m × 0.25 mm i.d., 0.5 µm film thickness, Phenomenex, Torrance, CA). The column initial temperature was 35 °C, which was held for 4 min and then raised to 230 °C at 4 °C/min, and held at 230 °C for 10 min. The carrier gas was helium with a flow rate of 1.5 mL/min and MS transfer line and ion source temperature were 280 and 230 °C, respectively. Electron ionization mass spectrometric data from m/z 40~350 were collected using a scan mode with an ionization voltage of 70 eV. Compound identification was achieved by comparing mass spectral data from the Wiley 275.L (G1035) database (Agilent Technologies, Santa Clara, CA).

The quantification ions for ethyl octanoate, ethyl butyrate, ethyl (±)-2-methyl butyrate; 2-phenyl-ethan-1, 1, 2, 2-ol, ethyl decanoate, linalool, α-terpineol, hexanoic acid, octanoic acid and decanoic acid in wine are listed in Table 3.1.

C₁₃-norisoprenoids potential

C₁₃-norisoprenoids exist in young wines as both free and bound forms, which can be released during aging. Since acid hydrolysis could accelerate this aroma releasing process, it can be used to evaluate the C₁₃-norisoprenoid potential of the wine. Two mL of the wine sample was mixed with 8 mL of citrate buffer (0.2 M, pH 2.5) and 10 µL of internal standard in a 20ml autosampler vial, then the vial was tightly capped the vial. The sample vials then were incubated in a 99 °C water bath for 1 hour. After incubation, the vial was cooled to room temperature for analysis. The samples analyzed using same SPME-GC-MS procedure as free -form volatile compound analysis.

Highly volatile compounds.

The concentration of acetaldehyde, ethyl acetate, isoamyl acetate, propanol, isobutyl and isoamyl alcohol are high in wine, so the quantification of these compounds was analyzed by Headspace- GC-FID method. In this method, sample headspace was

directly injected into the GC system and the compounds were detected by flame ionized detector. 0.5 mL of wine was pipetted into a 20 mL auto-sampler vial, diluted with 0.5 mL of milli-Q water. 20 μ L of the internal standard (2.5mg/mL of methyl propionate) was added to the sample. Then the vial was tightly capped with a Teflon-faced silicone septa. The extraction and injection were conducted by an autosampler (Gerstel, Linthicum, MD) equipped with a 1mL syringe. Before injection, the sample was incubated at 70 °C for 15 min with 250 rpm agitation. The syringe temperature was kept at 70 °C, and the injection volume was 0.5 mL. A DB-WAX (30m \times 0.25mm \times 0.5 μ m, Agilent Technologies, Palo Alto, CA) column was chosen for the separation of the analytes, the carrier gas was nitrogen at 2 mL/min. The initial oven temperature was 35°C, and held for 4 minutes, then increased to 150°C at a rate of 10°C /min, and held for 5 minutes. The inlet temperature was 200 °C and the split ratio of 1:10. The FID temperature was 250 °C. Identifications were conducted by comparing retention time with authentic pure standards.

Sulfur containing compounds.

The sulfur containing compounds were analyzed by a Varian CP-3800 gas chromatograph equipped with a pulsed-flame photometric detector (PFPD; Varian, Walnut Creek, CA). One mL of wine was pipetted into a 20 mL auto-sampler vial and diluted with 9 mL of saturated sodium chloride water with 2% ethanol. 20 μ L of 0.5 mg/L of ethyl methyl sulfide and 0.004 mg/L of diisopropyl disulfide were added into the vial, served as the internal standard. 50 μ L of 5% acetaldehyde solution was added to eliminate the interference of SO₂ to other sulfur containing compounds. The extraction and injection were conducted by an autosampler (Gerstel, Linthicum, MD) that equipped with a SPME fiber. Volatile sulfur containing compounds in headspace were extracted by a Carboxen-PDMS fiber (85 μ m, Supelco, Bellefonte, PA) at 30°C for 20 min using the autosampler. A DB-FFAP column (30m \times 0.32mm \times 1 μ m, Agilent Technologies) was used for separation with nitrogen as the carrier gas at a flow rate of 2mL/min. The initial oven temperature was 35 °C, and held for 3 min, then increased to 150°C at 10°C /min,

held at 150°C for 5 min, then ramped to 220 °C at 20 °C /min, held for 3 min. The PFPD was operated in sulfur mode, with 6 ms gate delay and 20 ms gate width. Identifications were made by comparing retention times with authentic pure standards

Volatile phenols

Due to the low concentration and low affinity to the SPME fiber, volatile phenolic compounds were difficult to detect by using the SPME method mentioned above, so benzene-derived compounds such as volatile phenols and methyl anthranilate were analyzed by SBSE-GC-MS method with an ethylene glycol–silicone (EG) coated stir bar (0.5 mm film thickness, 10 mm length, Gerstel Inc.,) (Zhou et al., 2015). 10 mL of wine sample was mixed with 10 mL of saturated NaCl in water. An aliquot of 20 µL internal standard (50 mg/L 3,4-dimethylphenol) was added. EG coated stir bar was placed into each vial and stirred for 3 hours at room temperature at 1000 rpm for extraction. After extraction, the EG stir bar was removed from the sample, rinsed with milli-Q water, dried with Kimtech wipers (Kimberly-Clark Professional Inc., Roswell, GA), then transferred into a thermal desorption unit (TDU) for GC-MS analysis. Analysis of volatile compounds was performed by a ZB-wax-plus capillary column (60 m × 0.25 mm i.d., 0.5 µm film thickness, Agilent Technologies,) on an Agilent 7890 gas chromatograph coupled with a Gerstel MPS-2 multipurpose TDU autosampler with a CIS-4 cooling injection system (Gerstel Inc.) and 5975 Mass selective detector. The analytes were first thermally desorbed at the TDU in splitless mode to release absorbed analytes, ramped from 25 to 220 °C at a rate of 100 °C/min, and held at 220 °C for 2 min. The CIS-4 was cooled to 35 °C during the sample injection, and then heated at 10 °C/s to 250 °C for 10 min. Solvent vent mode was used during the injection with a split vent flow of 50 mL/min. The oven program was set at 35 °C for 4 min, raised to 150 °C at 20 °C/min, and then raised to 230 °C at 4 °C/min, and held for 10 min. Helium served as the carrier gas with a constant flow of 1.5 mL/min for separation. The MS transfer line and ion source temperature were 280 °C and 230 °C, respectively. The mass selective detector in full scan mode was used to collect the data. Electron ionization mass spectrometric data from

m/z 35 to 300 were collected, with an ionization voltage of 70 eV. Identifications were made by comparing mass spectral data with the Wiley 275.L database (Agilent Technologies, Santa Clara, CA) and confirmed by authentic pure standards.

Calibration curves.

For each method above, internal standard calibration was obtained by the interpolation of relative peak areas in the calibration graphs. A standard curve was built with synthetic wine (3.5 g/L tartaric acid, 12% v/v ethanol, pH 3.5) containing known amounts of the analytes. Standard calibration curves were obtained through Chemstation software (Agilent Technologies, Santa Clara, CA). Standard curves were set up for each individual compound and were used to calculate the concentrations of volatile compounds in the samples respectively (Table 3.1).

3.3.6 Statistical analysis

Mean values were calculated. Treatment differences and interactions were analyzed using analysis of variance (ANOVA) with irrigation amount and irrigation frequency as the main factors using SPSS version 20 (IBM, Chicago, IL). Statistical differences among treatment levels were identified using Tukey's HSD mean separation at the $p < 0.05$ level.

3.4 Results

3.4.1 Total monomeric anthocyanin (TMA) and total phenolic (TP) analysis

The TMA and TP contents in wines were presented in Figure 3.1 and Figure 3.2. In 2015, TMA and TP content responded to different irrigation amounts similarly. For Malbec wine, the 35/70 treatment resulted in lower TMA and TP concentration. The 70/70 treatment resulted in the lowest TMA and TP contents in Syrah. For both Malbec and Syrah wine, the 70/35 treatment resulted in the highest levels of TMA and TP. In 2016, no differences were found among irrigation treatments in Malbec wines. Similar to

Syrah wine in 2015, the 70/35 treatment of 2016 Syrah wine resulted in the highest level of TMA content. The irrigation frequency had limited impact on TMA and TP in both Malbec and Syrah wines in 2015 and 2016.

3.4.2 Wine volatile profile

Table 3.2, 3.3, 3.4 and 3.5 showed the volatile profile of Malbec and Syrah wine of 2015 and 2016 respectively. Different irrigation amount treatment showed complicated impact on the aroma profile of the corresponding wines. Fermentation-derived volatile compounds such as esters and higher alcohols make up the majority of volatile compounds in wine.

3.4.2.1 Grape-derived volatile compounds

Terpenoids: The impacts of irrigation amount and frequency on terpenoids were presented in Tables 3.6 and 3.7. In general, irrigation frequency showed no impact on terpenoids level in Syrah wines, but influence terpenoids concentration in Malbec wines. Linalool, nerol and α -terpineol in Malbec wines with 1 \times irrigation frequency were significantly higher than wines made with grapes of 3 \times irrigation frequency treatments (Table 3.6a). Irrigation amount showed different influences on terpene concentration within Syrah and Malbec. For Malbec wines, irrigation amount showed impact on linalool, geraniol, α -terpineol and nerol, among which 70/35 irrigation amount resulted in a highest nerol level in both 2015 and 2016. Linalool, α -terpineol and nerol were significantly higher in 70/35 treatments than others in 2016, while geraniol level was higher in 35/70 and 35/35 irrigation treatment than 70/35 and 70/70 (Table 2.6b). Irrigation amount influenced the geraniol and β -citronellol levels in Syrah wines. Geraniol level was high in 35/70 and 35/35 irrigation treatment but low in 70/35 and 70/70 treatments in Syrah (Table 2.7b).

C₁₃-norisoprenoids: β -damascenone, β -ionone, TDN (1,1,6-trimethyl-1,2-dihydronaphthalene) and vitispirane are the most important C₁₃-norisoprenoids in wine.

As shown on tables 3.6 and 3.7, irrigation frequency did not show impact on both free form and bound form β -damascenone, β -ionone, vitispirane and TDN for either Malbec or Syrah. No impact on free form C_{13} -norisoprenoids in both Malbec and Syrah wines was found between different irrigation amount, meanwhile the bound form C_{13} -norisoprenoids concentration in Syrah wines were also not influenced by the irrigation amount (Table 3.6a and 3.7a). As shown on Table 3.6b, the 70/70 irrigation amount led to the higher bound form vitispirane and TDN levels in Malbec wines compared to all other treatments. The odor activity value (OAV) of β -damascenone and β -ionone in Malbec and Syrah wines are shown in Tables 3.10 and 3.11. Their OAV values were high in both Malbec and Syrah wine (OAV of β -damascenone >100 , OAV of β -ionone >3). The free vitispirane and TDN in experimental wines were below their sensory thresholds. However, after acid hydrolysis, the concentration of vitispirane and TDN increased dramatically, the concentration of TDN were above its threshold.

3.4.2.2 Fermentation-derived volatile compounds

Higher alcohols: As shown in Tables 3.10 and 3.11, isoamyl alcohol, isobutyl alcohol and Phenylethyl alcohol were found at concentrations higher than their respective sensory threshold value in the analyzed Malbec and Syrah wines (OAV >1). For both Syrah and Malbec wines, irrigation frequency showed no impact on higher alcohol level based on MANOVA analysis. However, the MANOVA showed significant effects of irrigation amount on Phenylethyl alcohol, 1-octanol, t-2-hexenol, propanol, isobutyl alcohol and isoamyl alcohol in Malbec wines, and propanol in Syrah wines. The 35/35 irrigation treatment contributed to a higher level of propanol, while 70/70 led to a low propanol concentration. This result was consistent in Syrah and Malbec wines. Consistent with trends found in Malbec grapes, the 1-octanol level was higher in wines made from 70/35 and 35/35 irrigation amount grapes, while the 70/35 irrigation amount showed relatively high benzyl alcohol concentration.

Ester: Neither branch-chained esters nor straight-chained esters in Syrah and Malbec wines were influenced by the irrigation frequency. Different irrigation amounts

showed no impacts on branch-chain esters in Malbec and Syrah. Significant differences were found in methyl anthranilate, ethyl acetate, ethyl decanoate and diethyl succinate in Malbec wines, while ethyl anthranilate, ethyl phenyl acetate and phenyl ethyl acetate were influenced by the irrigation amount in Syrah wines. As shown in Table 3.6b, the 35/35 irrigation contributed to higher ethyl acetate and diethyl succinate content, while the 70/70 irrigation treatment showed lower concentrations. Among esters shown in Tables 3.10 and 3.11, straight chain esters including ethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, diethyl succinate and isoamyl acetate in both Malbec and Syrah had concentrations higher than their sensory threshold (OAV>1). However, diethyl succinate and ethyl isobutyrate in Malbec wine in 2015 than 2016 had concentrations higher than their sensory threshold in 2015.

Fatty Acid: Hexanoic acid, octanoic acid and decanoic acid were identified in experimental wines in this study. The impact of regulated deficit irrigation on fatty acid composition in wine was dependent on variety and year. As shown in Tables 3.6 and 3.7, water management showed no impact on fatty acid concentration of Syrah wines for both 2015 and 2016. However, in 2016, 70/35 irrigation amount had the highest hexanoic and decanoic acid concentrations in Malbec wine, while 70/70 irrigation had the lowest. But these variations were not found in 2015 Malbec wines.

Other compounds: Aldehyde and volatile phenolic compounds in experimental wines quantified in this study were insensitive to the change of water status in grape vines. The irrigation frequency and irrigation amount all showed no impact on the acetaldehyde and guaiacol, p-cresol, m-cresol, eugenol and 4-vinyl guaiacol concentrations in both Malbec and Syrah wines.

3.4.3 Correlation between YAN and wine volatile profile

Figures 3.7, 3.8, 3.9, 3.10, 3.11, 3.12 and 3.13 showed the correlation between YAN level and ethyl acetate, ethyl butyrate, phenyl ethyl acetate, ethyl phenyl acetate, isoamyl acetate and ethyl isobutyrate in Malbec and Syrah wines. In both Malbec and

Syrah wines, straight chained esters, ethyl acetate, ethyl butyrate had a positive relationship with YAN. However, ethyl phenyl acetate and phenyl ethyl acetate, Phenylethyl alcohol and benzyl alcohol were negatively related to the YAN level in grape juice. The isoamyl alcohol and isobutyl alcohol concentration decreased in Malbec and Syrah with the increased of YAN level. This trend was consistent in all Malbec and Syrah wines. For branch-chained esters, ethyl isobutyrate showed a negative correlation with YAN level, with the increase of YAN concentration in grape must, ethyl isobutyrate concentration in wine decreased (Figure 3.12). Yet, the isoamyl acetate was found to increase with increasing YAN concentrations (Figure 3.13).

3.5 Discussion

TP and TMA: As being part of the grape-derived secondary metabolites in wine, considerable research has been conducted to investigate the plant water status on phenolic compounds in grape skin as they are significantly important to wine quality, conferring much of the color and structured properties of wine (Castellarin, 2007). The TP and TMA content in grape skin are extracted by water and alcohol during fermentation, and eventually influence the wine TP and TMA concentration. It was commonly reported that water stress had positive impacts on phenolic compound and anthocyanin concentrations (Roby, 2004; Koundouras, 2006). Yet, this trend was not observed in this study. In the experimental wines, a higher TMA level was found in the 70/35 irrigation treatment. Researchers had associated the increased anthocyanin concentration in grapes with smaller berry size. However, as berry weight was poorly correlated to anthocyanins and total phenolic concentration in this study, our research supported that the increased anthocyanins and phenolic concentrations under water deficit condition could not be influenced by the smaller berry size. The TP and TMA concentration in grape could be the results of interaction between cluster microclimate and favorable accumulation conditions in plant (Price et al., 1995; Koundouras et al., 2006). Since all the wines were made of frozen grapes, the phenolic and anthocyanins contents could be high due to the collapse of the cell wall during water crystallization. It was possible that the inconsistent

trends between years and varieties might be due to the different extraction ability of experimental wine, since during fermentation, the low YAN level in some wines led to a slow fermentation process. The grape must with low YAN concentration, for example, the 70/70 3× treatment in both variety had the lowest YAN level among all the treatments. Thus, it took three more days for the yeast to digest all the sugar content during fermentation process.

Terpenoids: Terpenoids are important volatile compounds contributing citrus and floral aromas to wines (Câmara et al., 2004). Typical aroma descriptions of some important terpenoids are floral, rose-like (geraniol, nerol, rose oxide), camphoraceous (linalool oxide), coriander (linalool) (Marais, 1983). Among terpenoids, linalool, geraniol, α -terpineol, nerol and β -citronellol are the most studied monoterpene alcohols in wines, and have great impact on Muscat wine aroma (Strauss et al., 1986). Syrah and Malbec are two neutral varieties, even though monoterpenes such as linalool, geraniol, α -terpineol, nerol and β -citronellol, can be found in grapes and their corresponding wines. Their concentration were below their sensory thresholds (OAV<1, Table 3.10 and Table 3.11). However, these compounds may still have synergic effects with other aroma compounds affecting wine aroma (Loscos et al., 2007). As described in Chapter 2, the free terpenoids in grape were low, however, the concentration of free terpenoids in wines increased compared to the free terpenoids in grapes due to the hydrolysis of bound form precursors in grapes.

In chapter 2, the free terpenoids in Malbec berries were not influenced by irrigation frequency, however, the terpenoid concentrations in the corresponding wines were affected by the irrigation frequency. Since the free terpenoids in wine were generated through free monoterpenes in grapes and the hydrolysis of monoterpenes precursors during fermentation, the variation could be due to the difference in bond-form monoterpenes in grape berries and extraction ability during wine production.

Other studies have been conducted to evaluate the influence of water deficit on terpenes in wine. Marais (1983) reported that irrigation significantly increase the terpene

concentration in Riesling wine. Ou and Qian (2010a) found that wines produced from Merlot vines under the water stress had higher concentrations of terpene alcohols, but the trend depended on the individual compound and vintage year. Fang et al. (2009) indicated that linalool, geraniol and citronellol were not influenced by water deficit treatments in Merlot wines. This discrepancy probably caused by the variety differences, weather and soil differences.

C₁₃-norisoprenoids: *C₁₃-norisoprenoids* have been identified as potential impact odorants in wines, contributing berry, honey and fruity notes in many red wines (Qian et al., 2009), especially β -damascenone and β -ionone (Ferreira et al., 2000; Gomez-Miguez et al., 2007). *C₁₃-norisoprenoids* are the degradation products of carotenoids and presented in grapes as both free and glycoside precursors. Studies had shown that glycoside precursors in grapes were converted to the free form *C₁₃-norisoprenoids* in wine during fermentation process (Kotseridis et al., 1999; Yuan and Qian, 2016). *C₁₃-norisoprenoids* presented in wine as both free and bound form. Free form *C₁₃-norisoprenoids* can be detected in young wines, while bound form *C₁₃-norisoprenoids* may be released by enzyme of acid hydrolysis during wine aging (Mendes-Pinto, 2009).

β -damascenone is a key odorant in wines, contributing a complex smell of honey and flora with an extremely low sensory threshold at 0.05 μ g/L in ethanol (Guth, 1997). In this study, the concentrations of free β -damascenone and β -ionone were higher than their sensory thresholds (OAV >1). β -ionone has a sweet and violet note in wines. It has a low perception sensory threshold of 0.09 μ g/L in synthetic wine (Winterhalter and Rouseff, 2002). The concentrations of β -ionone were low in the experimental wines in this study, but the concentrations of free β -ionone were still above its sensory threshold, ranging from 0.15 μ g/L to 0.20 μ g/L. After acid hydrolysis, the concentration of β -ionone increased, indicating the potential released of β -ionone during wine aging. Similar to what was found in bound form *C₁₃-norisoprenoids* in grape berries, neither irrigation amount nor irrigation frequency influenced the free and bound form β -ionone and β -damascenone for either Syrah or Malbec wines of 2015 and 2016. These results showed

that the bound C₁₃-norisoprenoids precursors from grape material during winemaking might be significantly related to the precursors found in grape berries. Further, the correlated hydrolytically-generated β -damascenone and β -ionone in grapes and free from β -damascenone, β -ionone in wines indicates that precursors in grape berries to these two compounds were significantly extracted during fermentation process, and the variation in grapes could lead to the final variation in wine.

TDN might had a negative influence on grape and wine flavor for its kerosene-like aroma. Vitispirane was another important odorant in wines. The concentration of free form vitispirane and TDN in Syrah and Malbec wines were below their threshold (vitispirane 800 μ g/L, TDN 20 μ g/L in model wine (Simpson et al., 1977;Sacks et al., 2012). In this study, unlike β -ionone and β -damascenone, the concentration of TDN and vitispirane in wines were not significantly associated with the levels of their acid hydrolysis precursors in the grapes. This relationship might suggest that the viticultural control of TDN and vitispirane may be less important than their release during fermentation process and wine aging (Ristic et al., 2010).

Higher alcohols and esters: Higher alcohols have strong and pungent smells, and they are believed to have negative effects on wine aroma when their concentrations are greater than 400 mg/L (Bakker and Clarke, 2011). Benzyl alcohol and 1-octanol in Syrah wines showed similar trend to those found in grapes, indicating that the benzyl alcohol and 1-octanol concentrations in wine were more related with their concentration in grapes. Esters including ethyl esters and acetates were mainly responsible for the fruity aromas in wine (Ferreira et al., 2000). Ethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, isoamyl acetate and ethyl isobutyrate were important esters found in experimental wines since their concentrations were above their sensory thresholds.

Esters, higher alcohols and volatile fatty acids are key odorants in the composition of wine aroma. These compounds are primary metabolites of yeast sugar and amino acid metabolism (Garde-Cerdán and Ancín-Azpilicueta, 2008). Studies has shown that the concentration of nitrogen source from must can influence the volatile composition of

wine (Garde-Cerdán and Ancín-Azpilicueta, 2008; Hernández-Orte et al., 2002; Hernández-Orte et al., 2006). Grape amino acids may serve as direct precursors of esters (Styger et al., 2011), indicating that the content of amino acids in grape must before fermentation would influence the formation of esters and higher alcohols. Phenylethyl alcohol, isobutyl alcohol and isoamyl alcohol were closely related to the amino acids concentrations in grapes (Rossouw et al., 2009).

In this study, the concentration of isoamyl alcohol, isobutyl alcohol decreased with the increase of the YAN, which were consistent with Hernandez's results (P Hernández-Orte et al., 2006). However, higher benzyl alcohol and Phenylethyl alcohol content were found with lower amount of YAN, which were on the contrary to Hernandez's results (Hernández-Orte et al., 2006). This difference is probably because the YAN level only presented the total nitrogen level instead of individual amino acids content. Phenylethyl alcohol and benzyl alcohol are generated from aromatic amino acids like phenylalanine and tyrosine (Rossouw et al., 2009), even though the YAN levels were high in grapes, the aromatic amino acids that the yeast used to generated these volatile compounds, such as phenylalanine, might be low in grape berries. Fermaid K used in winemaking process added additional amino acids into the grape must, which will be the possible cause of this discrepancy. Even though Fermaid K provide additional amino acids to the yeast growth, but due to the same amount of amino acids added in to the fermentor, the correlation of YAN and volatile can still be observed. To better understand how YAN level in grapes influence the volatile compositions in wine, wines fermented without addition nitrogen source are needed. Correlation were also found between YAN level and two branch-chained esters in wine, ethyl butyrate and isoamyl acetate. Branch-chained esters were closely related with the branch-chained amino acids in grape.

As presented in Chapter 2, 70/70 irrigation amount led to the lowest YAN level and the higher YAN level was achieved by 35/35 irrigation amount in 2015 and 2016's Syrah grapes and 2015's Malbec grapes. Comparing the wine data, 35/35 irrigation contributed a higher YAN level in grape must, leading a higher ethyl acetate, isoamyl

acetate but lower isoamyl alcohol, isobutyl alcohol, Phenylethyl alcohol, phenethyl acetate, ethyl phenyl acetate and ethyl isobutyrate content in 2016's Syrah and Malbec wines and 2015' Syrah wines. Apparently, irrigation treatment influenced the YAN concentration in grape juice, then the YAN level altered the volatile profile of wine. This proved that the final wine aroma could be altered by manipulating vine's water status in vineyard.

3.6 Summary

Few studies have studied how vineyard water management practices influence the volatile composition of wine. Results from this study demonstrated that regulated deficit irrigation in the vineyard influenced wine volatile profiles. Irrigation frequency showed little influence on Malbec wine, but no impact on Syrah wine quality. However, irrigation amount appeared to have greater influence on volatile composition of final wine compared to irrigation frequency. Grape compositions were influenced by the water status of grapevine. Thus, the grape-derived volatile compounds were changed with the irrigation amount. Moreover, regulated deficit irrigation changed the content of yeast assimilable nitrogen (YAN) in grape must before fermentation, leading the differences of the fermentation-derived volatile composition in corresponding wines. In both Malbec and Syrah wines, total straight chained esters, ethyl acetate, ethyl butyrate had a positive relationship with YAN. However, ethyl phenyl acetate and phenyl ethyl acetate had similar performance with Phenylethyl alcohol and benzyl alcohol, having negative relationship with YAN level. Smaller amounts of isoamyl alcohol and isobutyl alcohol were formed with higher concentrations of amino acids in the juice. In summary, the volatile composition of wine can be influenced by the vine water status.

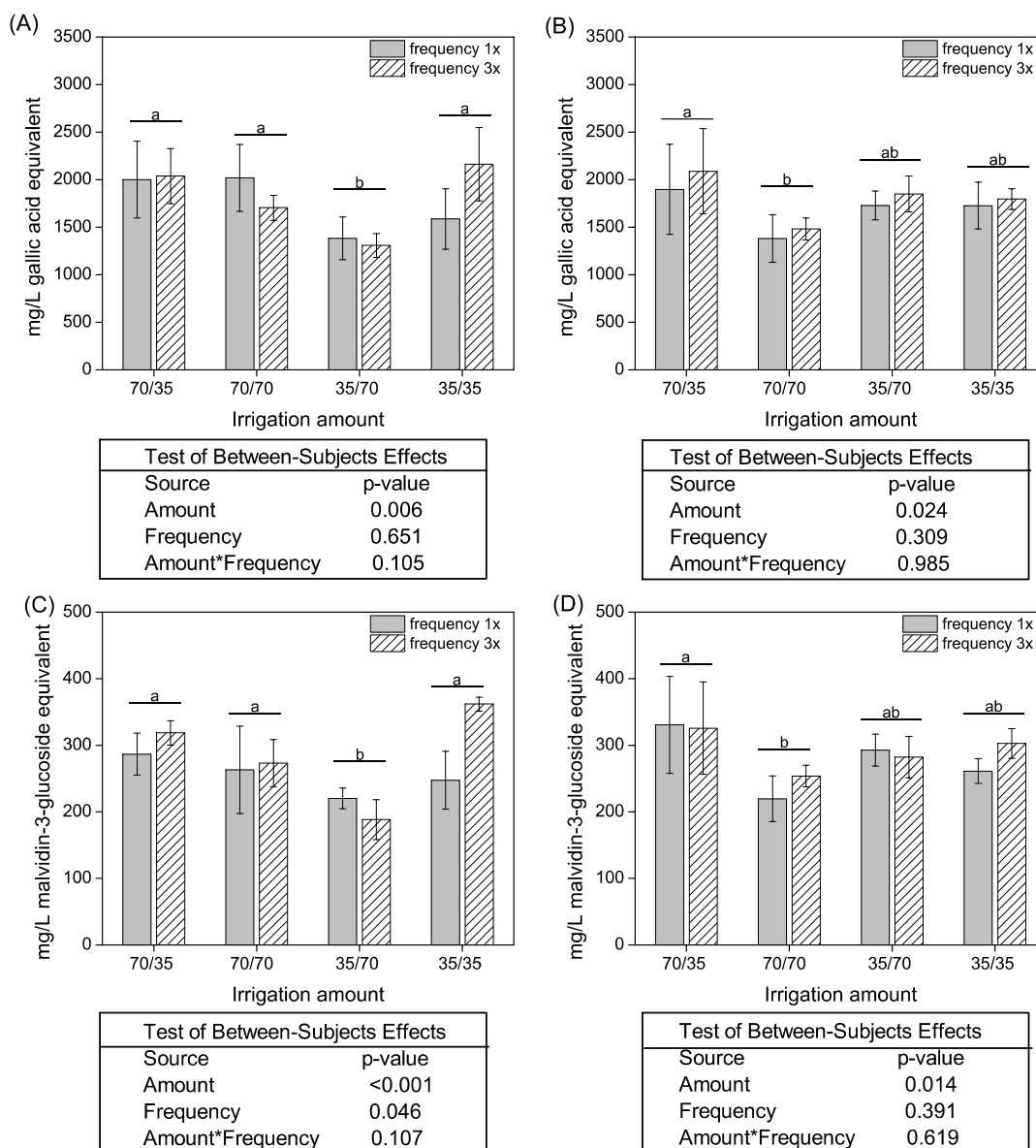


Figure 3.1. Total monomeric anthocyanin and total phenolic content in 2015 Malbec and Syrah wines from different irrigation treatments

(A) total phenolic in Malbec; (B) total phenolic in Syrah; (C) total anthocyanins in Malbec; (D) total anthocyanins in Syrah. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means.

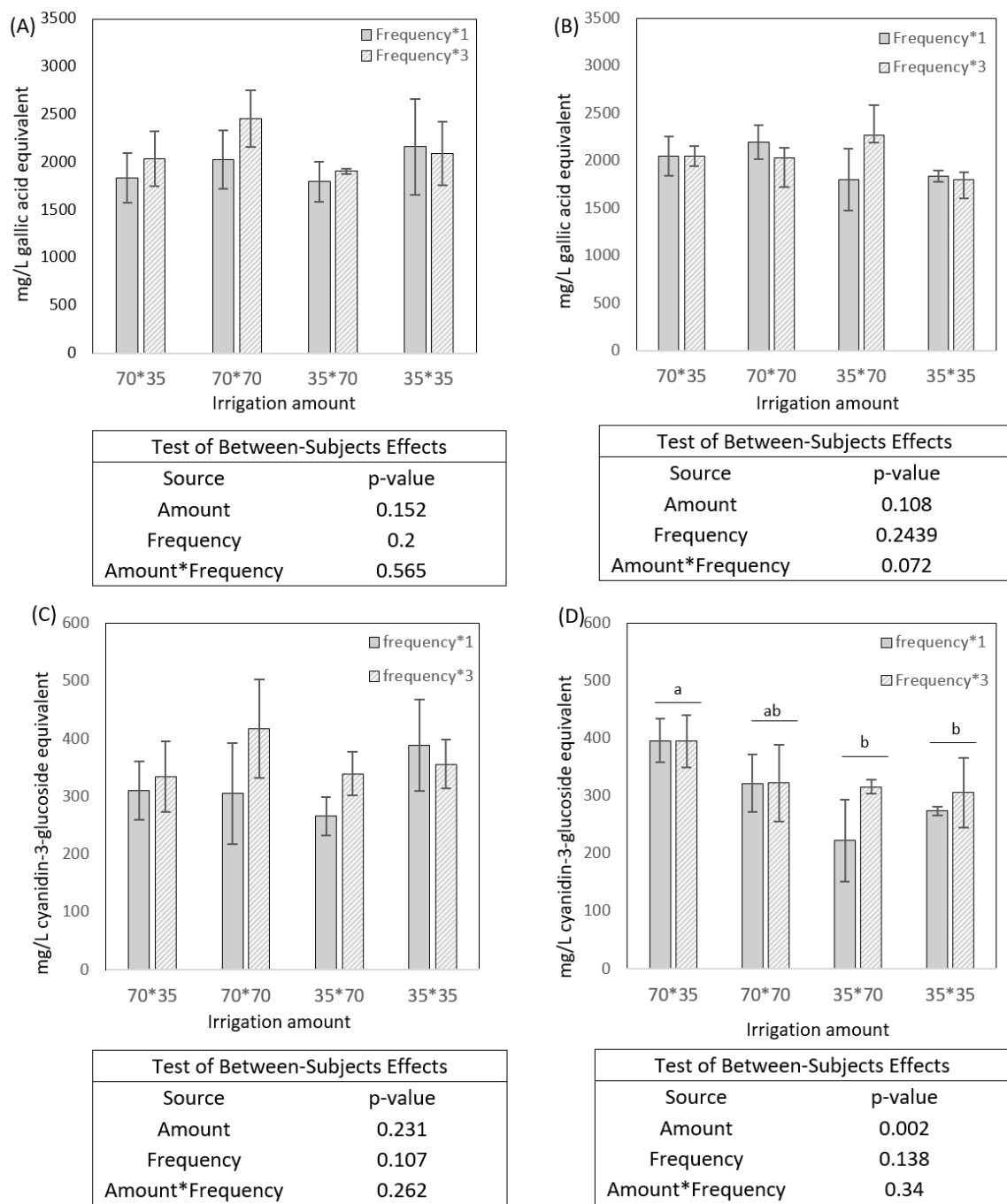


Figure 3.2. Total monomeric anthocyanin and total phenolic content in 2016 Malbec and Syrah wines from different irrigation treatments

(A) total phenolic in Malbec; (B) total phenolic in Syrah; (C) total anthocyanins in Malbec; (D) total anthocyanins in Syrah. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means.

Table 3.1. Selected quantification ions for isotope volatile compounds in wine

Compounds	Quantify ion	Equation	Regression correlation coefficient
ethyl butyrate-4,4,4-d3 (IS)	74		
ethyl butyrate	71	resp.ratio = 0.808×amt.ratio + 0.047	0.9986
ethyl isobutyrate	71	resp.ratio = 0.508×amt.ratio	0.9980
isobutyl acetate	56	resp.ratio = 0.396×amt.ratio	0.9994
ethyl octanoate-d15 (IS)	91		
ethyl octanoate	88	resp.ratio = 0.693×amt.ratio	0.9999
methyl octanoate	87	resp.ratio = 0.483×amt.ratio	0.9844
octyl acetate	70	resp.ratio = 0.631×amt.ratio	0.9982
octyl butyrate	112	resp.ratio = 0.299×amt.ratio	0.9935
ethyl hexanoate-d11 (IS)	91		
ethyl hexanoate	88	resp.ratio = 0.832×amt.ratio + 0.006	0.9996
hexyl acetate	84	resp.ratio = 0.303×amt.ratio	0.9987
(±)-linalol-d3(vinyl-d3) (IS)	124		
linalool	121	resp.ratio = 0.365×amt.ratio	0.9999
nerol	93	resp.ratio = 0.912×amt.ratio	0.9986
geraniol	123	resp.ratio = 0.461×amt.ratio	0.9998
alpha-terpineol-d3 (IS)	124		
α-terpineol	121	resp.ratio = 0.822×amt.ratio	0.9992
β-citronellol	123	resp.ratio = 0.97×amt.ratio	0.9878
2-phenyl-d5-ethan-1,1,2,2-d4-ol (IS)	131		
Phenylethyl alcohol	122	resp.ratio = 0.825×amt.ratio + 0.046	0.9936
benzyl alcohol	108	resp.ratio = 1.203×amt.ratio	0.9989
hexanol	69	resp.ratio = 1.184×amt.ratio	0.9906
1-octanol	84	resp.ratio = 0.196×amt.ratio	0.9985
1-octen-3-ol	85	resp.ratio = 3.714×amt.ratio	0.9991
β-damascenone	121	resp.ratio = 0.455×amt.ratio	0.9980
β-ionone	177	resp.ratio = 0.032×amt.ratio	0.9955
Vitispirane ^a	192	resp.ratio = 0.455×amt.ratio	0.9980
TDN ^a	157	resp.ratio = 0.455×amt.ratio	0.9980
hexanoic-d11 acid (IS)	77		
hexanoic acid	73	resp.ratio = 2.652×amt.ratio	0.9993
octanoic-d15 acid (IS)	77		
octanoic acid	73	resp.ratio = 2.33×amt.ratio	0.9986
decanoic-d19 acid (IS)	77		
decanoic acid	73	resp.ratio = 2.29×amt.ratio	0.9984
ethyl decanoate-d19 (IS)	105		
ethyl decanoate	101	resp.ratio = 0.394×amt.ratio	0.9982
diethyl succinate	129	resp.ratio = 0.076×amt.ratio	0.9877
phenyl ethyl acetate	91	resp.ratio = 0.201×amt.ratio + 0.004	0.9949
ethyl phenyl acetate	164	resp.ratio = 0.476×amt.ratio	0.9915

(Table 3.1 continued)

ethyl (±) -2-	107		
methylbutyrate-d9 (IS)			
ethyl-2-methyl butyrate	102	resp.ratio = 1.084×amt.ratio	0.9955
methyl-2-methyl butyrate	101	resp.ratio = 0.3×amt.ratio	0.9959
butyl-2-methyl butyrate	103	resp.ratio = 0.108×amt.ratio	0.9997

a: The standard curve of β -damascenone was used for calculation

Table 3.2. Free volatile composition of 2015 Malbec wine produced from different treatments ($\mu\text{g/L}$)

Irrigation Amount Irrigation Frequency	70/35		70/70		35/70		35/35	
	1×	3×	1×	3×	1×	3×	1×	3×
<i>Esters</i>								
<i>Straight-Chain Esters</i>								
methyl octanoate	2.16±0.51	1.96±0.50	1.98±0.13	1.60±0.39	2.06±0.23	1.86±0.47	2.28±0.45	1.93±0.19
methyl anthranilate	0.23±0.10	0.24±0.14	0.15±0.07	0.19±0.04	0.17±0.01	0.15±0.09	0.19±0.04	0.21±0
Ethyl anthranilate	0.48±0.13	0.41±0.18	0.31±0.18	0.25±0.10	0.18±0.01	0.18±0.08	0.32±0.22	0.28±0.14
ethyl acetate ^a	28.1±1.7	22.7±7.0	25.4±5.7	21.9±3.1	29.0±3.2	28.1±4.0	29.7±6.7	30.3±4.1
ethyl butyrate	171±58	113±49	121±7	96±45	110±18	129±13	146±14	143±17
ethyl hexanoate	384±127	278±121	296±20	241±61	286±14	273±43	348±45	295±16
ethyl octanoate	275±69	191±120	218±18	167±94	214±25	213±26	226±24	194±25
ethyl decanoate	101±16	82±39	89±9	78±29	105±4	102±11	99±9	91±6
ethyl phenyl acetate	4.56±1.22	3.49±0.79	3.32±0.40	3.92±2.53	2.97±0.60	3.07±1.08	3.50±1.05	2.95±0.19
hexyl acetate	8.2±3.8	10.4±4.1	8.7±5.8	7.9±2.4	9.2±4.6	6.2±2.1	10.8±0.6	6.0±3.0
octyl butyrate	8.12±0.40 a	7.32±0.32 ab	6.87±0.08 b	6.92±0.93 ab	7.09±0.39 b	7.26±0.36 ab	7.07±0.17 b	6.73±0.53 b
diethyl succinate	2505±348 ab	2747±103 a	2098±116 ab	2260±388 ab	1936±308 b	1805±88 b	2216±338 ab	2253±401 ab
phenyl ethyl acetate	38.1±8.8	35.7±2.9	32.4±6.4	42.9±20.3	27.1±4.4	28.2±6.4	31.4±12.7	28.0±5.5
<i>Branched-Chain Esters</i>								
ethyl isobutyrate	53.6±15.9	28.2±25.5	43.2±2.1	47.9±2.4	39.3±9.6	44.7±6.5	48.5±7.7	41.3±5.1
isobutyl acetate	40.1±13.6	26.0±10.3	28.8±3.7	38.2±7.2	26.7±8.8	31.6±4.7	36.2±11.2	30.0±7.0
Isoamyl acetate	949±34	652±309	753±208	808±204	893±42	851±128	860±86	737±179
ethyl-2-methyl butyrate	8.38±3.47	6.23±1.48	6.18±0.38	7.70±1.94	6.36±1.83	6.64±1.56	7.53±2.43	6.24±1.69
methyl-2-methyl butyrate	34.4±12.4	27.7±5.8	26.5±4.0	39.1±2.5	28.6±0.6	26.9±1.5	31.1±1.8	29.2±11.2
butyl-2-methyl butyrate	1.00±0.26	0.98±0.46	0.70±0.04	0.74±0.08	0.70±0.04	0.67±0.02	0.82±0.09	0.78±0.11
<i>Alcohols</i>								
Propanol ^a	30.2±3.3	27.8±3.1	24.3±7.8	22.4±5	32.6±5.6	31.3±4.6	30.7±10.0	32.0±11.8
Isobutyl alcohol ^a	29.6±2.1	29.8±3.4	27.9±6.1	39.9±8.4	33.1±5.0	31.5±4.3	31.1±12.8	23.5±0.9
Isoamyl alcohol ^a	223±19	216±23	185±45	253±40	218±18	214±40	217±69	176±15
Phenylethyl alcohol ^a	29.3±6.1	29.3±6.1	29.3±6.1	29.3±6.1	23.8±3.7	29.3±6.1	29.3±6.1	29.3±6.1
benzyl alcohol	164±24	163±13	169±35	139±10	150±29	138±7	132±7	153±5

(Table 3.2 continued)

hexanol	805±66	797±100	603±58	531±120	650±5	553±131	883±7	961±365
1-octanol	17.5±0.5 a	15.4±2.8 ab	15.7±0.3 ab	12.6±2.1 b	14.8±1.4 ab	15.0±1.9 ab	17.0±0.2 a	16.6±1.3 ab
trans-2-hexen-1-ol	12.9±0.4 a	10.6±0.2 b	9.5±0.2 bc	10.7±0.4 b	9.3±0 bc	8.8±0 c	9.2±1.1 bc	8.8±0.8 c
Terpenoids								
α-terpineol	2.90±0.31	2.76±0.30	2.51±0.41	2.76±0.55	2.53±0.39	2.83±0.32	2.59±0.64	2.65±0.69
β-citronellol	26.2±2.7	20.5±9.0	25.9±1.5	21.5±8.0	21.5±5.5	21.6±2.7	23.9±1.1	25.2±2.5
linalool	8.42±1.02	7.20±1.10	7.17±0.52	8.13±0.47	7.42±0.74	7.48±0.65	7.92±0.73	7.42±0.89
nerol	6.94±0.34 a	5.57±0.06 abc	6.53±0.61 ab	5.27±0.79 bc	4.63±0.28 c	4.58±0.64 c	5.47±0.73 abc	5.30±0.71 abc
geraniol	16.9±2.6	14.3±3.0	17.8±1.6	13.5±1.8	17.5±5.4	18.3±1.2	17.5±1.6	17.0±1.7
C₁₃-Norisoprenoids								
beta-damascenone	3.07 ± 0.35	2.4 ± 0.58	2.89 ± 0.2	2.43 ± 0.83	2.51 ± 0.65	2.84 ± 0.09	2.64 ± 0.35	2.69 ± 0.1
beta-ionone	0.24 ± 0.05	0.16 ± 0.06	0.17 ± 0.04	0.14 ± 0.04	0.09 ± 0.08	0.15 ± 0.03	0.16 ± 0.01	0.2 ± 0.04
vitispirane	6.11 ± 0.02	6.08 ± 0.02	5.99 ± 0.1	6.04 ± 0.1	6.09 ± 0.09	6.11 ± 0.05	6.35 ± 0.32	6.03 ± 0.13
TDN	7.6 ± 0.3	7.15 ± 0.29	7.41 ± 0.79	6.97 ± 0.9	7.43 ± 0.77	7.98 ± 0.33	7.18 ± 0.59	7.14 ± 0.46
Aldehydes								
Acetaldehyde ^a	13.9±2.8	10.1±1.6	16.8±7.4	11.8±6.0	9.1±1.2	7.3±1.2	10.5±3.7	10.7±1.5
Acids								
hexanoic acid	568±10	437±130	571±45	444±146	547±24	592±51	581±40	565±34
octanoic acid	1298±35	901±490	1359±67	951±484	1329±100	1412±147	1300±49	1204±30
decanoic acid	222±15	176±56	230±17	177±43	232±10	233±30	214±5	208±4
Volatile phenolic compounds								
guaiacol	4.54±1.16	6.83±1.34	4.95±1.50	4.86±0.73	4.56±0.02	3.76±0.85	5.91±3.34	6.24±0.53
p-cresol	1.00±0.09	1.07±0.24	0.93±0.48	1.09±0.19	0.96±0.08	1.06±0.02	0.96±0.16	1.35±0.13
m-cresol	0.33±0.04	0.61±0.23	0.35±0.02	0.33±0.01	0.33±0.01	0.30±0.03	0.40±0.17	0.40±0.03
eugenol	1.16±0.18	1.01±0.35	1.11±0.15	0.99±0.02	0.92±0.28	0.89±0.03	0.77±0.24	1.10±0.09
4-vinylguaiacol	20.4±4.2	24.2±4.2	20.8±3.3	17.5±0.7	15.8±4.4	18.6±4.3	21.6±7.5	28.4±2.8
Sulfur Containing Compounds								
MeSOAc	1.29±0.31	0.68±0.52	1.04±0.15	1.11±0.51	1.17±0.22	1.36±0.27	1.33±0.21	1.77±0.62
Methionol ^b	2197±425	1786±330	2486±377	2796±724	3901±1436	2370±1188	2150±677	1858±560

Mean ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n=3$ independent field samples). ^a: Concentration expressed as mg/L. ^b: Concentration expressed as peak area. ^c: vitispirane and TDN estimated on the basis of β-damascenone

Table 3.3. Free volatile composition of 2016 Malbec wine produced from different treatments ($\mu\text{g/L}$)

Irrigation Amount Irrigation Frequency	70/35		70/70		35/70		35/35	
	1×	3×	1×	3×	1×	3×	1×	3×
<i>Esters</i>								
<i>Straight-chain esters</i>								
methyl octanoate	2.00±0.45	2.80±0.40	1.60±0.58	0.80±0.69	2.30±0.36	2.30±0.91	0.90±1.51	1.40±0.81
methyl anthranilate	24.5±19.2 a	5.1±2.7 ab	3.0±2.5 b	2.5±1.5 b	1.9±2.3 b	2.3±0.9 b	1.7±0.5 b	1.5±0.8 b
ethyl anthranilate	75.2±82.5	12.3±8.5	6.2±4.4	7.1±3.5	8.6±6.3	3.7±2.3	5.2±2.3	5.1±0.7
ethyl acetate ^a	56.5±8.6 ab	69.0±10.8 ab	53.3±12.8 ab	42.0±5.5 b	76.5±33.0 ab	61.8±19.4 ab	68.8±8.8 ab	91.6±11.4 a
ethyl butyrate	116±27	171±36	129±43	86±17	154±28	179±15	91±47	155±47
ethyl hexanoate	333±74	505±79	360±95	315±109	444±31	458±55	208±213	357±118
hexyl acetate	8.2±3.8	10.4±4.1	8.7±5.8	7.9±2.4	11.3±4.8	12.8±11.6	4.8±19.7	6.0±3.0
ethyl octanoate	207±73	267±25	198±74	183±62	242±21	235±34	115±85	154±61
ethyl decanoate	119±21 ab	153±23 a	111±21 ab	73±9 b	127±18 ab	100±19 ab	51±39 ab	84±27 b
ethyl phenyl acetate	2.60±1.18 ab	2.20±0.35 b	2.80±0.75 ab	5.40±2.49 a	2.90±0.85 ab	2.90±0.55 ab	1.90±0.78 ab	1.30±0.40 b
octyl butyrate	7.60±0.17	7.30±0.29	7.70±0.44	7.00±1.73	7.60±0.15	6.90±0.20	4.60±0.45	7.00±0.10
diethyl succinate	712±38	853±85	737±184	675±111	831±42	785±44	644±45	952±197
phenyl ethyl acetate	43.5±12.7	38.0±6.3	38.6±6.1	60.3±17.0	43.0±8.6	46.7±19.1	28.0±13.0	28.1±4.9
<i>Branched-chain esters</i>								
ethyl isobutyrate	11.0±4.7	12.7±8.1	14.1±5.0	16.0±0.8	13.9±1.4	14.6±1.8	10.2±2.3	10.5±1.8
isobutyl acetate	21.1±5.0	26.1±4.5	24.1±7.6	21.2±1.7	27.8±2.3	27.4±1.6	19.6±4.4	19.7±0.3
Isoamyl acetate	344±138	378±172	369±132	364±131	358±181	358±206	729±315	498±240
methyl-2-methyl butyrate	25.2±6.0	28.4±12.1	26.4±8.2	18.3±6.9	20.8±5.3	17.3±15.1	25.4±0	24.6±8.2
butyl-2-methyl butyrate	0.80±0.21 ab	1.10±0.21 ab	0.80±0.15 ab	0.50±0.4 b	1.20±0.21 ab	1.10±0.12 ab	1.25±0.21 a	0.90±0.40 ab
<i>Alcohols</i>								
Phenylethyl alcohol	41.4±6.3 ab	36.0±6.6 abc	41.4±3.6 ab	41.4±3.0 a	41.4±4.2 bc	41.4±1.5 abc	41.4±9.9 abc	24.2±6.2 c
benzyl alcohol	237±62	238±53	207±17	161±23	224±50	247±66	160±24	274±7
hexanol	3361±2365	1736±2020	2156±1557	2217±2171	1817±2249	2016±463	1999±339	1828±415
1-octanol	20.8±1.2 b	25.2±2.2 ab	20.7±1.8 ab	17.6±2.2 ab	25.4±3.0 a	24.6±2.2 a	16.6±4.1 ab	23.5±4.9 a
1-octen-3-ol	nd	6.23±1.84	6.81±1.08	6.00±1.56	9.03±2.22	9.48±0.92	6.32±6.16	13.50±4.50
trans-2-hexen-1-ol	8.78±0.69	8.79±0.47	9.59±0.59	9.07±0.54	7.82±1.00	8.41±0.69	9.64±0.73	8.91±1.43

(Table 3.3 Continued)

Propanol ^a	28.4±7.8 ab	33.6±7.5 ab	23.6±4.4 b	16.5±2.50 b	32.9±8.3 ab	33.9±6.1 ab	31.8±7.2 ab	45.9±6.3 a
Isobutyl alcohol ^a	23.3±3.5 bc	20.0±2.6 bc	28.1±4.8 ab	31.6±1.6 a	22.1±4.4 bc	19.9±0.8 bc	18.9±2.0 c	17.9±0.7 c
Isoamyl alcohol ^a	258±47 bc	236±35 bc	290±29 ab	359±24 a	227±34 bc	234±8.97 bc	235±42 bc	193±26 c
Terpenoids								
linalool	35.7±5.3 a	15.6±1.5 b	11.2±1.7 bc	10.2±1.6 bc	7.5±0.7 c	7.5±0.3 c	8.6±0.3 c	7.5±0.7 c
nerol	14.5±2.4 a	11.4±0.9 ab	9.4±1.6 bc	7.0±2.8 bc	4.8±0.4 c	5.4±0.7 c	4.9±2.3 c	5.7±1.1 c
geraniol	4.2±0.7 c	11.7±0.9 bc	11.4±3.1 bc	15.7±5.3 ab	29.3±3.4 a	23.9±3.4 ab	15.8±5.6 ab	22.6±3.8 ab
alpha-terpineol	7.60±0.26 a	4.30±0.26 b	3.80±0.53 b	4.30±0.67 b	3.40±0.21 b	3.40±0.15 b	2.80±0.22 b	3.60±0.45 b
beta-citronellol	35.4±8.3	33.8±3.5	25.4±7.5	28.0±5.8	31.2±1.9	37.9±1.4	18.7±3.8	27.1±6.8
C₁₃-Norisoprenoids								
beta-damascenone	5.04 ± 0.9	5.03 ± 0.21	4.48 ± 1.09	5.19 ± 0.83	4.41 ± 0.56	3.89 ± 0.61	4.5 ± 0.55	3.88 ± 0.34
beta-ionone	0.25 ± 0.12	0.42 ± 0.08	0.28 ± 0.14	0.35 ± 0.1	0.51 ± 0.11	0.46 ± 0.07	0.43 ± 0.15	0.3 ± 0.11
vitispirane	nd	6.09 ± 0.12	6.48 ± 0.15	6.28 ± 0.65	6.46 ± 0.13	nd	6.09 ± 0.67	6.24 ± 0.19
TDN	6.41 ± 0.68	6.65 ± 0.41	6.26 ± 0.52	6.84 ± 0.36	7.31 ± 0.91	7.17 ± 0.45	7.44 ± 0.87	6.71 ± 0.6
Aldehydes								
Acetaldehyde	68.5±11.4	50.8±12.8	63.3±26.7	54.4±19.9	82.3±14.0	47.4±11.6	38.8±10.4	54.6±16.5
Acids								
hexanoic acid	1013±116 ab	1185±93 a	905±109 ab	767±41 b	1124±83 ab	963±217 ab	629±235 ab	792±144 ab
octanoic acid	1468±418	1922±44	1347±424	1132±183	1681±169	1552±241	926±351	1114±337
decanoic acid	226±38 abc	307±23 a	203±28 abc	143±15 c	269±25 ab	221±49 abc	120±56 bc	182±43 bc
Volatile phenolic compounds								
guaiacol	7.5±1.4	4.8±0.5	5.1±1.3	7.8±2.8	5.8±4.3	10.8±10.0	7.0±1.6	8.4±3.8
p-cresol	1.7±1.4 ab	0.8±0.1 b	0.8±0.2 b	0.9±0.2 ab	1.4±1.2 ab	0.8±0.1 b	0.8±0.2 ab	2.8±0.5 a
m-cresol	1.70±1.07	0.90±0	0.90±0.32	1.10±0.42	0.80±0.38	1.00±0.26	1.00±0.21	1.10±0.12
eugenol	3.20±2.84	1.70±0.55	1.30±0.44	1.50±0.66	3.30±3.07	1.50±0.31	2.10±1.02	1.70±0.32
4-vinyl-guaiacol	31.0±16.6	13.9±2.7	18.7±7.0	24.1±8.4	21.3±18.2	27.8±19.0	27.8±4.9	54.7±36.2
Sulfur containing compounds								
DMS	17.1±2.5 a	13.9±4.7 ab	13.9±2.2 ab	11.7±0.1 ab	11.6±1.0 ab	11.3±1.5 ab	11.3±2.9 ab	10.1±0.6 b
Methionol ^b	50.4±46.5	50.4±4.4	50.4±3.4	50.4±2.6	50.4±5.7	50.4±7.1	15.6±3.3	50.4±3.6

Mean ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n=3$ independent field samples). ^a: Concentration expressed as mg/L. ^b: Concentration expressed as peak area. ^c: vitispirane and TDN estimated on the basis of β -damascenone

Table 3.4. Free volatile composition of 2015 Syrah wine produced from different treatments ($\mu\text{g/L}$)

Irrigation Amount Irrigation Frequency	70/35		70/70		35/70		35/35	
	1 \times	3 \times	1 \times	3 \times	1 \times	3 \times	1 \times	3 \times
<i>Esters</i>								
<i>Straight-chain esters</i>								
methyl octanoate	2.01 \pm 0.31	2.59 \pm 2.35	1.78 \pm 0.24	1.99 \pm 0.44	1.92 \pm 0.29	1.54 \pm 0.16	1.61 \pm 0.10	1.51 \pm 0.19
methyl anthranilate	0.32 \pm 0.10 ab	0.25 \pm 0.10 ab	0.32 \pm 0.15 ab	0.57 \pm 0.34 a	0.31 \pm 0.19 b	0.48 \pm 0.14 ab	0.21 \pm 0.18 b	0.35 \pm 0.11 ab
ethyl anthranilate	0.53 \pm 0.21 ab	0.56 \pm 0.08 ab	0.33 \pm 0.02 b	0.75 \pm 0.48 a	0.43 \pm 0.17 b	0.75 \pm 0.28 ab	0.45 \pm 0.10 ab	0.32 \pm 0.19 b
ethyl acetate ^a	32.4 \pm 9.8	33.3 \pm 9.3	30.3 \pm 10.6	28.5 \pm 1.6	37.6 \pm 5.1	41.5 \pm 3.7	42.2 \pm 6.2	40.3 \pm 5.1
ethyl butyrate	187 \pm 32	175 \pm 27	150 \pm 40	173 \pm 24	197 \pm 7	202 \pm 24	204 \pm 10	220 \pm 21
ethyl hexanoate	313 \pm 3	300 \pm 38	321 \pm 29	347 \pm 93	338 \pm 50	328 \pm 78	282 \pm 24	312 \pm 51
ethyl octanoate	200 \pm 7	173 \pm 27	197 \pm 15	213 \pm 30	179 \pm 12	164 \pm 18	158 \pm 17	166 \pm 21
ethyl decanoate	94.8 \pm 19.0	65.7 \pm 18.7	88.3 \pm 14.0	92.2 \pm 12.9	82.6 \pm 3.6	80.1 \pm 5.3	77.6 \pm 12.4	74.9 \pm 4.8
ethyl phenyl acetate	2.95 \pm 1.35	3.42 \pm 1.10	3.21 \pm 1.36	4.08 \pm 1.46	2.13 \pm 0.46	1.72 \pm 0.47	1.77 \pm 0.58	2.03 \pm 0.51
hexyl acetate	1.96 \pm 0.75	6.59 \pm 0.58	8.32 \pm 2.31	8.15 \pm 6.51	4.70 \pm 0.62	3.48 \pm 1.94	4.30 \pm 0.33	4.53 \pm 0.31
octyl butyrate	6.44 \pm 0.66	6.97 \pm 0.25	5.49 \pm 2.68	7.76 \pm 0.87	7.00 \pm 0.11	6.54 \pm 1.28	6.84 \pm 0.37	6.70 \pm 0.12
diethyl succinate	2339 \pm 278	1854 \pm 586	1622 \pm 163	1775 \pm 350	1518 \pm 49	1885 \pm 200	1585 \pm 379	1732 \pm 144
phenyl ethyl acetate	23.6 \pm 8.3 ab	46.0 \pm 24.2 ab	47.3 \pm 17.5 ab	67.4 \pm 32.3 a	28.9 \pm 4.3 ab	22.9 \pm 0.6 b	25.2 \pm 5.5 ab	29.6 \pm 5.4 ab
<i>Branched-chain esters</i>								
ethyl isobutyrate	38.5 \pm 15.0	32.0 \pm 2.1	36.9 \pm 6.4	36.8 \pm 6.9	30.9 \pm 4.3	26.4 \pm 2.3	26.2 \pm 2.7	29.1 \pm 9.4
isobutyl acetate	34.1 \pm 9.1	46.9 \pm 10.3	51.5 \pm 3.2	59.4 \pm 12.3	44.7 \pm 3.3	41.3 \pm 5.4	44.5 \pm 3.8	49.0 \pm 9.1
Isoamyl acetate	1373 \pm 481	1805 \pm 603	1455 \pm 216	1812 \pm 344	1463 \pm 93	1431 \pm 61	1310 \pm 400	1719 \pm 289
ethyl-2-methyl butyrate	7.42 \pm 2.32	5.54 \pm 3.22	2.30 \pm 1.99	7.49 \pm 3.68	3.91 \pm 1.55	2.32 \pm 0.58	2.95 \pm 1.15	2.14 \pm 1.90
methyl-2-methyl butyrate	28.6 \pm 3.9 a	18.7 \pm 10.4 ab	15.7 \pm 1.1 ab	14.3 \pm 0 ab	0 \pm 0 b	16.7 \pm 14.5 ab	21.2 \pm 1.9 ab	28.8 \pm 10.1 a
butyl-2-methyl butyrate	0.77 \pm 0.11	0.70 \pm 0.12	0.73 \pm 0.04	0.80 \pm 0.15	0.88 \pm 0.11	0.82 \pm 0.22	0.73 \pm 0.06	0.81 \pm 0.14
<i>Alcohols</i>								
Phenylethyl alcohol	27.3 \pm 11.0	31.3 \pm 10.1	32.2 \pm 11.3	37.0 \pm 3.1	24.4 \pm 4.7	17.9 \pm 1.9	24.2 \pm 0.7	16.0 \pm 1.6
benzyl alcohol	192 \pm 19	184 \pm 27	134 \pm 24	160 \pm 36	174 \pm 21	170 \pm 20	180 \pm 32	180 \pm 11
hexanol	1212 \pm 127	1190 \pm 91	1344 \pm 219	1164 \pm 98	1044 \pm 83	1084 \pm 157	1208 \pm 224	1141 \pm 80
trans-2-hexen-1-ol	10.8 \pm 0.9 a	10.1 \pm 0.7 ab	10.4 \pm 1.4 ab	9.5 \pm 0.4 abc	9.2 \pm 0.7 abc	8.2 \pm 0.2 abc	7.3 \pm 0.5 c	8.0 \pm 0.4 bc

(Table 3.4 Continued)

1-octanol	16.0±3.1	14.3±0.8	15.7±1.4	14.9±1.5	15.6±0.5	15.4±0.4	15.1±1.5	15.0±0.8
Propanol ^a	29.8±6.6	27.9±5.9	26.4±8.4	23.6±1.9	31.9±1.6	37.0±3.0	37.3±6.3	33.8±2.7
Isobutyl alcohol ^a	26.0±7.0	30.4±8.1	36.7±14.2	36.8±1.4	26.1±4.8	22.4±1.1	24.4±2.0	23.0±2.4
Isoamyl alcohol ^a	205±61	227±61	252±63	271±1	202±49	178±16	183±26	169±16
Terpenoids								
linalool	6.91±1.17	6.45±0.83	7.81±0.27	7.58±0.36	8.23±0.96	7.92±0.36	7.09±0.97	7.46±0.79
nerol	3.66±0.70 b	5.09±0.51 ab	3.22±2.80 b	4.17±0.60 ab	4.84±1.01 ab	4.49±0.73 ab	6.70±2.12 a	4.80±0.53 ab
geraniol	16.7±2.4	19.5±2.4	18.3±4.3	21.1±2.5	23.9±0.4	21.8±1.0	22.9±3.1	23.2±2.8
α-terpineol	4.01±2.45	2.60±0.18	2.90±0.38	3.02±0.15	3.20±0.27	3.33±0.43	3.83±1.51	5.48±4.24
β-citronellol	28.2±0.8	30.0±8.7	22.2±1.5	25.4±3.9	28.3±0.6	25.4±2.1	28.9±5.1	28.4±6.9
C₁₃-Norisoprenoids								
β-damascenone	1.61 ± 0.68	1.8 ± 0.45	2.85 ± 0.7	2.43 ± 0.33	2.01 ± 0.28	1.92 ± 0.3	1.99 ± 0.37	1.88 ± 0.36
β-ionone	0.19 ± 0.04	0.22 ± 0.01	0.19 ± 0.04	0.19 ± 0.01	0.17 ± 0	0.19 ± 0.03	0.2 ± 0.02	0.2 ± 0.02
vitispirane	6.19 ± 0.13	6.08 ± 0.08	6.15 ± 0.25	6.29 ± 0.36	6.13 ± 0.02	6.23 ± 0.16	6.10 ± 0.06	6.09 ± 0.01
TDN	8.04 ± 0.32 a	7.37 ± 0.58 ab	7.49 ± 0.84 ab	7.76 ± 0.65 a	7.27 ± 0.14 ab	6.23 ± 0.22 b	4.55 ± 3.94 ab	6.83 ± 0.55 ab
Aldehydes								
acetaldehyde	7.05±0.91	9.58±1.19	7.41±0.53	5.39±2.83	7.26±0.35	7.11±1.07	10.07±3.77	8.93±0.80
Acids								
hexanoic acid	511±2 ab	411±24 b	547±49 a	488±24 ab	519±65 ab	454±6 ab	463±43 ab	425±29 ab
octanoic acid	1110±41 ab	895±128 b	1195±65 a	1131±59 ab	1188±90 ab	1045±45 ab	1039±95 ab	950±74 ab
decanoic acid	189±29	135±27	171±9	172±16	177±5	154±10	149±15	129±18
Volatile phenolic compounds								
guaiacol	13.9±3.2	14.1±2.3	10.7±5.9	15.1±3.2	19.0±1.7	18.8±6.9	17.2±5.2	16.0±2.3
p-cresol	0.81±0.32	0.68±0.46	0.57±0.29	0.57±0.12	0.69±0.17	0.58±0.21	0.63±0.13	0.66±0.32
m-cresol	0.45±0.07	0.41±0.04	0.36±0.06	0.46±0.08	0.49±0.03	0.46±0.06	0.46±0.06	0.42±0.03
eugenol	0.93±0.19	0.94±0.08	0.86±0.17	0.95±0.12	1.00±0.04	0.91±0.08	0.99±0.12	0.87±0.16
4-vinylguaiacol	8.7±1.8	8.6±1.2	12.1±7.5	7.9±2.6	10.7±1.2	12.9±3.6	13.0±2.7	11.6±0.7
Sulfur containing compounds								
H ₂ S	0.37±0.16 a	0.34±0.10 ab	nd	0.08±0 bc	0.07±0.02 c	0.08±0.04 c	0.05±0.01 c	0.08±0.02 bc
DMS	0.38±0.38	0.99±0.49	0.37±0.26	0.49±0.16	1.26±1.29	2.16±1.55	2.97±3.40	1.27±0.62

(Table 3.4 Continued)

MeSOAc	2.63±1.92	4.33±0.95	5.11±1.83	9.19±3.71	6.52±2.47	5.46±2.83	7.28±2.57	3.90±2.70
EtSOAc	0.06±0.05	0.14±0.06	0.10±0.04	0.19±0.07	0.07±0	0.09±0.05	0.08±0.02	0.14±0.12
Methionol ^b	794±925 ab	1353±908 ab	2112±903 ab	2899±559 a	853±479 ab	373±181 b	479±365 b	325±337 b

Mean ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means (n=3 independent field samples).

^a: Concentration expressed as mg/L. ^b: Concentration expressed as peak area. ^c: vitispirane and TDN estimated on the basis of β -damascenone

Table 3.5 Free volatile composition of 2016 Syrah wine produced from different treatments ($\mu\text{g/L}$)

Irrigation Amount Irrigation Frequency	70/35		70/70		35/70		35/35	
	1×	3×	1×	3×	1×	3×	1×	3×
<i>Esters</i>								
<i>straight-chain esters</i>								
methyl octanoate	2.72±0.59	1.31±0.52	1.44±0.75	1.72±0.35	2.02±0.68	2.75±0.21	2.13±1.54	1.56±0.67
methyl anthranilate	0.97±0.4	0.73±0.37	0.78±0.06	0.80±0.59	1.55±1.28	0.55±0.40	0.39±0.23	0.59±0.61
ethyl anthranilate	2.70±1.07	1.81±0.01	2.65±0.38	4.79±2.29	4.34±1.19	2.33±2.35	1.13±0.56	1.59±1.25
ethyl acetate ^a	58.1±3.4 b	55.1±16.9 b	51.9±13.8 b	40.9±3.0 c	64.5±6.0 b	105.5±16.7 a	73.1±23.6 ab	58.3±7.9 b
ethyl butyrate	222±111	169±38	165±63	139±41	225±144	385±7	269±153	236±77
ethyl hexanoate	555±216	396±109	445±145	439±88	646±258	696±183	926±688	543±167
ethyl octanoate	312±118	208±102	224±95	230±91	322±88	380±27	261±145	219±114
ethyl decanoate	137±31	93±40	113±33	86±20	108±34	162±14	136±55	111±18
ethyl phenyl acetate	1.90±1.01	1.98±0.47	1.99±0.46	2.25±0.37	2.18±0.35	1.21±0.22	1.31±0.42	1.28±0.41
diethyl succinate	478±44 ab	508±45 ab	517±45 ab	345±30 b	658±139 a	552±184 ab	549±56 ab	502±69 ab
hexyl acetate	16.6±12.0	16.1±10.7	10.4±5.3	19.3±7.3	14.7±11.8	20.6±4.2	15.9±10.9	13.9±7.4
octyl butyrate	7.82±0.15	7.48±0.79	7.57±0.27	7.15±1.28	7.63±0.45	7.36±0.29	7.40±0.34	7.62±0.23
phenyl ethyl acetate	50.8±21.2	61.9±25.2	55.1±12.1	57.8±6.0	47.6±4.0	36.3±2.3	34.3±2.7	33.5±4.8
<i>branched-chain esters</i>								
ethyl isobutyrate	14.8±3.4 ab	15.9±12.7 a	13.2±2.6 ab	12.6±7.3 ab	12.5±4.3 ab	17.8±1.9 ab	10.3±3.8 b	10.6±2.7 b
Isoamyl acetate	547±253	471±228	614±214	390±113	559±196	924±128	582±410	340±206
isobutyl acetate	31.2±16.5	24.8±7.9	25.8±14.0	21.2±8.7	31.5±20.2	51.9±5.5	35.1±19.2	29.7±8.7
methyl-2-methyl butyrate	26.0±5.0	27.8±5.3	12.3±12.8	18.8±11.7	29.2±11.3	28.0±5.4	26.8±4.4	33.5±7.6
butyl-2-methyl butyrate	1.07±0.64	0.87±0.21	0.86±0.3	0.89±0.18	1.45±0.77	1.63±0.29	1.39±0.69	1.09±0.29
<i>Alcohols</i>								
Phenylethyl alcohol	41.7±1.5	39.7±2.3	41.2±2.5	36.6±2.6	42.9±1.8	39.0±3.3	37.0±4.4	36.3±2.7
benzyl alcohol	258±33	265±52	256±22	216±20	271±20	281±17	272±12	217±2
hexanol	2274±262	2451±154	1913±584	2414±266	2757±254	2806±506	2373±361	2712±622
1-octanol	22.6±2.2 ab	21.0±1.6 b	20.7±3.4 b	22.6±0.2 ab	26.3±3.5 ab	29.6±2.0 a	24.1±3.5 ab	22.9±3.2 ab
1-octen-3-ol	6.51±1.55 ab	7.73±1.25 ab	4.10±3.56 b	7.23±0.93 ab	10.57±1.13 a	9.23±2.29 ab	8.56±3.14 ab	8.39±2.68 ab

(Table 3.5 Continued)

Propanol ^a	29.7±9.7 bc	31.8±9.3 bc	34.5±5.5 bc	22.5±2.2 c	42.4±12.3 abc	57.4±4.9 a	50.8±10.9 ab	40.0±3.7 abc
Isobutyl alcohol ^a	27.6±8.3	31.9±3.3	33.9±2.4	32.9±1.9	34.7±4.2	27.1±4.6	28.5±5.2	32.5±6.2
Isoamyl alcohol ^a	244±84	283±67	322±23	282±40	354±35	294±82	251±46	301±52
Terpenoids								
α-terpineol	2.67±0.24	2.53±0.20	2.29±0.27	2.43±0.05	3.16±1.27	3.17±0.12	1.60±1.22	2.52±0.33
β-citronellol	31.6±5.4 ab	35.3±3.3 ab	36.2±2.8 ab	36.2±6.3 ab	40.3±7.7 a	34.7±6.8 ab	27.6±3.6 ab	21.3±4.5 b
linalool	6.91±0.03	6.61±0.39	5.63±0.27	5.92±0.27	6.90±2.76	6.79±0.43	5.32±0.63	5.76±0.64
nerol	2.82±0.43	3.47±0.75	3.61±0.87	3.02±0.35	3.77±2.79	3.49±1.17	2.99±0.96	3.42±1.16
geraniol	9.7±1.4 b	7.5±2.5 b	9.1±2.0 b	8.3±1.3 b	12.5±4.7 ab	17.1±1.1 a	11.3±3.9 ab	9.8±1.4 b
C₁₃-Norisoprenoids								
β-damascenone	4.89 ± 0.17	4.3 ± 0.19	3.03 ± 0.62	4.75 ± 0.9	5.02 ± 1.43	3.18 ± 0.51	3.98 ± 1.23	4.92 ± 1.28
β-ionone	0.25 ± 0.1	0.21 ± 0.06	0.18 ± 0.06	0.26 ± 0.08	0.35 ± 0.03	0.33 ± 0.01	0.2 ± 0.08	0.2 ± 0.08
vitispirane	6.39 ± 1.05 bc	7.8 ± 0.52 abc	5.98 ± 0.35 c	8.31 ± 0.27 abc	9.06 ± 1.04 a	7.45 ± 0.57 abc	6.66 ± 1.05 abc	8.43 ± 1.46 ab
TDN	6.76 ± 0.77	4.97 ± 4.36	7.42 ± 1.5	7.27 ± 0.69	7.41 ± 0.25	6.69 ± 0.58	6.77 ± 0.53	7.03 ± 0.59
Aldehydes								
Acetaldehyde ^a	52.5±11.4	31.9±5.0	28.8±13.1	41.4±9.9	64.8±40.8	46.8±10.2	69.0±33.5	68.4±16.1
Acids								
hexanoic acid	1327±333	938±383	883±186	913±102	1140±298	1700±237	1466±631	1408±195
octanoic acid	1803±593	1151±459	1237±451	1347±423	1587±316	2171±114	1606±734	1442±479
decanoic acid	235±58 ab	151±54 b	175±49 ab	157±33 ab	199±41 ab	302±19 a	252±92 ab	217±40 ab
Volatile phenolic compounds								
guaiacol	18.4±6.1	36.9±15.3	18.7±0.6	30.6±7.3	35.6±19.3	22.1±0.4	28.5±4.6	24.6±1.6
p-cresol	1.19±0.46	1.27±0.44	1.04±0.17	1.06±0.36	0.73±0.05	0.81±0.18	0.83±0.22	1.54±0.69
m-cresol	0.85±0.06	1.00±0.17	1.01±0.28	0.98±0.12	1.03±0.21	1.00±0.08	0.92±0.04	0.92±0.08
eugenol	1.89±0.58	1.54±0.19	2.21±0.63	1.64±0.30	1.97±0.62	2.12±1.11	1.42±0.31	1.07±0.10
4-Vinylguaiacol	8.75±1.86	8.56±2.47	9.66±6.30	10.99±4.69	8.62±8.35	6.28±7.79	5.31±0.60	3.62±1.46
Sulfur Containing Compounds								
DMS	12.6±3.6	10.3±0.8	9.4±0.3	9.8±1.2	9.9±1.2	12.4±0.4	10.0±1.3	9.6±0.9
MeSOAc	2.31±0.59	1.62±0.84	2.49±0.71	1.25±0.39	2.25±1.20	2.73±0.49	1.45±0.24	1.40±0.38
DMTS	0.04±0	0.04±0.01	0.04±0	0.05±0.02	0.06±0.02	0.06±0.01	0.06±0.01	0.05±0.01

(Table 3.5 Continued)

Methionol ^b	5590±1186 b	4550±2485 b	6181±1116 ab	4441±1367 b	6388±1412 ab	6214±1313 ab	7109±957 ab	10033±1488 a
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Mean ± SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means (n=3 independent field samples). ^a:

Concentration expressed as mg/L. ^b: Concentration expressed as peak area. ^c: vitispirane and TDN estimated on the basis of β -damascenone

Table 3.6a Composition of volatile compounds in MALbec wines with vineyard water management from 2015 to 2016

<i>Compound</i>	Mean values^a				<i>p</i>-values^b				
	Year		Irrigation frequency		Year	Year × Irrigation Amount	Irrigation Amount	Irrigation Frequency	Irrigation Amount × Frequency
	2015	2016	1×	3×					
<i>Esters</i>									
<i>Straight-chain esters</i>									
methyl octanoate	1.74	1.92	1.97	1.69	ns	ns	ns	ns	ns
methyl anthranilate	0.19	5.33	3.98	1.54	0.001	0.007	0.006	ns	ns
ethyl anthranilate	0.3	15.4	12.1	3.7	0.017	ns	ns	ns	ns
Ethyl acetate ^a	26.7	65.0	45.8	45.9	<0.001	ns	0.003	ns	ns
ethyl butyrate	122	138	130	130	ns	ns	ns	ns	ns
ethyl hexanoate	293	400	353	340	0.001	ns	ns	ns	ns
ethyl octanoate	205	212	217	200	ns	ns	ns	ns	ns
ethyl decanoate	91	107	104	95	0.019	ns	0.031	ns	ns
ethyl phenyl acetate	3.41	2.84	3.09	3.16	ns	ns	ns	ns	0.047
hexyl acetate	8.8	10.4	9.9	9.3	ns	ns	ns	ns	ns
octyl butyrate	7.17	7.25	7.37	7.04	ns	ns	ns	ns	ns
diethyl succinate	2220	814	1493	1541	<0.001	0.001	0.001	ns	ns
phenyl ethyl acetate	32.8	43.4	37.7	38.5	0.002	ns	ns	ns	0.025
<i>Branch-chained esters</i>									
Isoamyl acetate	793	425	637	581	<0.001	ns	ns	ns	ns
isobutyl acetate	28.4	23.9	27.4	24.9	ns	ns	ns	ns	ns
ethyl isobutyrate	39.8	13.2	28.0	25.0	<0.001	ns	ns	ns	ns
methyl-2-methyl butyrate	27.2	21.2	23.6	24.8	ns	ns	ns	ns	ns
Butyl-2-methyl butyrate	0.71	0.89	0.83	0.77	ns	ns	ns	ns	ns
<i>Alcohols</i>									
Phenylethyl alcohol ^a	27.1	37.6	32.6	32.1	<0.001	ns	<0.001	ns	ns
Benzyl alcohol	151	229	191	189	<0.001	0.019	ns	ns	ns

(Table 3.6 Continued)

hexanol	714	2079	1399	1393	<0.001	ns	ns	ns	ns
1-octanol	15.5	22.8	19.5	18.8	<0.001	ns	0.002	ns	ns
trans-2-hexenol	9.94	8.54	9.22	9.26	0.001	ns	0.002	ns	ns
Propanol ^a	29.1	30.8	29.5	30.4	ns	ns	<0.001	ns	ns
Isobutyl alcohol ^a	30.4	22.7	26.4	26.8	<0.001	ns	0.001	ns	0.039
Isoamyl alcohol ^a	211	254	229	235	<0.001	0.014	0.001	ns	0.005
Terpenoids									
linalool	6.9	12.6	11.3 a	8.2 b	<0.001	<0.001	<0.001	<0.001	<0.001
nerol	5.28	8.07	7.29 a	6.06 b	<0.001	<0.001	<0.001	0.008	0.036
geraniol	16.5	17.5	16.9	17.1	ns	<0.001	<0.001	ns	ns
α -terpineol	2.70	4.33	3.69 a	3.34 b	<0.001	<0.001	<0.001	0.007	<0.001
β -citronellol	23.0	31.0	27.0	27.0	<0.001	ns	ns	ns	ns
Volatile phenolic compounds									
guaiacol	5.26	7.16	5.72	6.70	0.049	ns	ns	ns	ns
p-cresol	1.07	1.23	1.07	1.23	ns	ns	ns	ns	0.003
m-cresol	0.38	1.06	0.72	0.73	<0.001	ns	ns	ns	ns
eugenol	0.99	2.05	1.74	1.30	0.003	ns	ns	ns	ns
4-vinyl guaiacol	21.0	27.4	22.3	26.1	ns	ns	ns	ns	ns
Aldehydes									
Acetaldehyde ^a	12.4	57.5	37.8	32.0	<0.001	ns	ns	ns	ns
Acids									
Hexanoic acid	529	968	778	718	<0.001	0.017	0.050	ns	ns
Octanoic acid	1182	1462	1371	1274	0.003	ns	ns	ns	ns
Decanoic acid	207	218	220	206	ns	0.007	0.009	ns	ns
C₁₃-Norisoprenoids									
β -damascenone	2.68	4.55	4.44	4.13	<0.001	ns	ns	ns	ns
β -ionone	0.17	0.37	0.35	0.34	0.007	ns	ns	ns	0.041
vitispirane	6.07	6.26	6.27	6.17	ns	ns	ns	ns	ns
TDN	7.36	6.85	6.92	6.90	ns	ns	ns	ns	ns

(Table 3.6 Continued)

*C*₁₃-Norisoprenoids after acid hydrolysis

β-damascenone	29.4	54.8	53.1	49.4	<0.001	ns	ns	ns	0.031
β-ionone	0.16	0.42	0.37	0.41	<0.001	ns	ns	ns	ns
vitispirane	69.3	80.0	81.0	76.1	ns	0.029	0.004	ns	ns
TDN	105	243	232	208	<0.001	<0.001	<0.001	ns	ns

a Means with different letters between year or irrigation frequency columns within a row differ significantly at $p \leq 0.05$ by Tukey HSD t test. ns indicates not significant
 b Results from a mixed model analysis of variance with year, irrigation amount, Irrigation frequency and their interactions as fixed effects. ^a: Concentration expressed as mg/L ^c:vitispirane and TDN estimated on the basis of β-damascenone

Table 3.6b Composition of volatile compounds in Malbec wines with vineyard water management from 2015 to 2016 (ug/L)

Year Irrigation Amount	2015				2016			
	70/35	70/70	35/70	35/35	70/35	70/70	35/70	35/35
<i>Esters</i>								
methyl anthranilate	0.24±0.11	0.17±0.06	0.16±0.06	0.20±0.03	8.10±4.60 a	2.78±1.85 ab	2.13±1.57 ab	1.60±0.61 b
Ethyl acetate ^a	25.4±5.4	23.7±4.5	28.6±3.0	30.0±5.0	62.8±11.1 ab	47.7±10.8 b	69.2±25.5 ab	80.2±15.4 a
ethyl decanoate	92±29	83±20	104±8	95±8	136±27 a	92±25 b	113±22 ab	89±31 b
diethyl succinate	2626±265 a	2179±271 b	1870±165 b	2234±332 ab	782±97 b	706±140 b	808±46 ab	959±128 a
<i>Terpenoids</i>								
linalool	7.8±1.2	7.6±0.6	7.5±0.5	7.7±0.8	25.7±11.6 a	10.7±1.6 b	7.5±0.5 b	8.1±0.8 b
nerol	6.3±0.8 a	5.9±0.9 a	4.6±0.4 ab	5.4±0.7 b	13.0±2.3 a	8.2±2.4 b	5.1±0.6 c	6.0±1.7 bc
geraniol	15.6±2.9	15.7±2.8	17.9±2.6	17.3±1.5	8.0±4.2 b	13.6±7.2 b	26.6±4.3 a	21.9±4.3 a
α-terpineol	2.83±0.28	2.63±0.45	2.68±0.32	2.62±0.60	5.95±1.82 a	4.07±0.61 b	3.47±0.16 b	3.83±0.43 b
<i>Alcohols</i>								
Phenylethyl alcohol ^a	28.9±4.6	31.2±5.9	24.8±5.7	24.6±7.9	38.7±6.5 ab	47.6±4.4 a	34.4±3.1 b	29.5±9.4 b
Benzyl alcohol	164±17	154±29	144±15	142±12	237±51 ab	184±31 b	236±54 ab	261±21 a
1-octanol	16.4±2.1	14.2±2.2	14.9±1.4	16.8±0.8	23.0±2.9 ab	19.2±2.5 b	25.0±2.4 a	24.0±4.1 ab
trans-2-hexenol	11.8±1.3 a	10.1±0.7 b	9.1±0.3 b	9.0±0.9 b	8.8±0.5	9.3±0.6	8.1±0.8	9.3±1.1
Propanol ^a	29.0±3.2 ab	23.3±3.9 b	31.9±3.9 a	33.4±2.8 a	31.0±7.4 ab	20.1±5.0 b	33.4±6.6 a	38.9±9.8 a
Isobutyl alcohol ^a	29.7±2.5	33.9±9.3	32.3±3.6	27.3±9.1	21.7±3.3 b	29.9±3.7 a	21.0±3.0 b	18.4±1.4 b
Isoamyl alcohol ^a	220±19	219±53	216±26	197±50	247±39 b	325±45 a	230±23 b	214±39 b
<i>Acids</i>								
Hexanoic acid	502±110	508±119	570±42	573±34	1099±133 a	836±106 b	1044±171 ab	893±206 ab
Decanoic acid	199±45	203±41	233±19	211±5	266±52 a	173±38 b	245±44 ab	189±45 b
<i>C₁₃-norisoprenoids after acid hydrolysis</i>								
vitispirane	67.1 ± 8.7	73.7 ± 10.6	68.9 ± 17.2	67.7 ± 9.2	62.7 ± 8.2 b	88.5 ± 14 a	79.8 ± 4.7 a	89 ± 9.7 a
TDN	115 ± 23	118 ± 20	102 ± 29	86 ± 17	164 ± 23 c	287 ± 41 a	229 ± 15 b	290 ± 47 a

a Means within columns among irrigation rows within each year followed by different letters differ significantly at $p \leq 0.05$ by Tukey HSD t test.

^a: Concentration expressed as mg/L. ^c: Vitispirane and TDN estimated on the basis of β-damascenone

Table 3.7a Composition of volatile compounds in Syrah wines with vineyard water management from 2015 to 2016 (ug/L)

Compound	Mean values ^a				<i>p-values</i> ^b				
	Year		Irrigation frequency		Year	Year × Irrigation Amount	Irrigation Amount	Irrigation Frequency	Irrigation Amount × Frequency
	2015	2016	1×	3×					
Esters									
<i>Straight-Chain Esters</i>									
methyl octanoate	1.87	1.96	1.95	1.87	ns	ns	ns	ns	ns
methyl anthranilate	0.35	0.80	0.61	0.54	0.040	0.027	ns	ns	ns
ethyl anthranilate	0.52	2.71	1.52 b	1.61 a	<0.001	0.021	0.026	0.001	0.015
ethyl acetate ^a	35.8	63.4	48.8	50.4	<0.001	ns	ns	ns	0.033
ethyl butyrate	188	226	202	212	ns	ns	ns	ns	ns
ethyl hexanoate	318	581	478	420	0.032	ns	ns	ns	ns
ethyl octanoate	181	270	232	219	0.002	ns	ns	ns	ns
ethyl phenyl acetate	2.67	1.76	2.18	2.25	ns	ns	0.011	ns	ns
ethyl decanoate	82	118	105	96	0.004	ns	ns	ns	ns
hexyl acetate	5.2	15.9	9.6	11.8	<0.001	ns	ns	ns	ns
octyl butyrate	6.72	7.50	7.03	7.19	0.004	ns	ns	ns	ns
diethyl succinate	1789	514	1158	1144	<0.001	ns	ns	ns	ns
phenyl ethyl acetate	36.4	47.2	39.1	44.4	<0.001	0.001	<0.001	ns	<0.001
<i>Branched-Chain Esters</i>									
Isoamyl acetate	1546	553	988	1112	<0.001	ns	ns	ns	ns
isobutyl acetate	46.4	31.4	37.3	40.5	ns	ns	ns	ns	ns
ethyl isobutyrate	32.1	13.1	23.7	23.7	0.001	ns	ns	ns	ns
methyl-2-methyl butyrate	18.0	25.0	20.2	23.5	0.002	ns	ns	ns	ns
butyl-2-methyl butyrate	0.78	1.15	0.99	0.94	0.009	ns	ns	ns	ns
<i>Terpenoids</i>									
linalool	7.43	6.20	6.84	6.90	ns	ns	ns	ns	ns
nerol	4.62	3.34	3.95	4.04	0.004	ns	ns	ns	ns
geraniol	20.9	10.7	15.5	16.0	<0.001	ns	0.019	ns	ns
α-terpineol	3.55	2.55	2.96	3.14	ns	ns	0.654	ns	ns
β-citronellol	27.1	32.9	30.4	29.6	0.030	ns	0.008	ns	ns

(Table 3.7a Continued)

C₁₃-Norisoprenoids

β-damascenone	2.06	4.26	4.03	3.81	<0.001	ns	ns	ns	0.001
β-ionone	0.19	0.25	0.24	0.24	ns	0.006	ns	ns	ns
vitispirane	6.16	7.50	6.90	7.64	0.003	ns	ns	ns	<0.001
TDN	7.24	7.12	7.06	7.09	ns	ns	ns	ns	ns

Alcohols

Phenylethyl alcohol ^a	26.3	39.3	33.9	31.7	<0.001	ns	ns	ns	ns
Benzyl alcohol	172	255	217	209	<0.001	0.023	ns	ns	ns
hexanol	1173	2462	1766	1870	<0.001	ns	ns	ns	ns
1-octanol	15.3	23.7	19.5	19.5	<0.001	ns	ns	ns	ns
Propanol ^a	31.0	38.6	35.4	34.2	0.022	ns	0.008	ns	0.023
Isobutyl alcohol ^a	28.2	31.1	29.7	29.6	ns	ns	ns	ns	ns
Isoamyl alcohol ^a	211	291	252	251	0.003	ns	ns	ns	ns

Acid

Hexanoic acid	477	1222	857	842	<0.001	ns	ns	ns	ns
Octanoic acid	1069	1543	1346	1266	0.002	ns	ns	ns	ns
Decanoic acid	160	211	193	177	0.005	ns	ns	ns	ns

Volatile phenolic compounds

guaiacol	15.6	27.5	20.3	22.3	0.004	ns	ns	ns	ns
p-cresol	0.65	1.06	0.81	0.90	0.009	ns	ns	ns	ns
m-cresol	0.44	0.96	0.69	0.71	<0.001	ns	ns	ns	ns
eugenol	0.93	1.74	1.41	1.25	0.001	ns	ns	ns	ns
4-vinyl guaiacol	10.7	7.6	9.6	8.8	0.003	0.047	ns	ns	ns

Aldehydes

Acetaldehyde	7.9	50.4	30.9	27.4	<0.001	ns	ns	ns	ns
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Sulfur containing compounds

Methionol ^b	1148	6313	3688	3773	<0.001	0.003	ns	ns	ns
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C₁₃-Norisoprenoids After acid hydrolysis

β-damascenone	29.7	47.6	45.9	44.6	<0.001	ns	ns	ns	ns
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(Table 3.7a Continued)

β -ionone	0.19	0.31	0.29	0.30	ns	0.010	ns	ns	ns
vitispirane	167	233	217	233	ns	ns	ns	ns	ns
TDN	204	659	585	610	<0.001	ns	ns	ns	ns

a Means with different letters between year or irrigation frequency columns within a row differ significantly at $p \leq 0.05$ by Tukey HSD t test. ns indicates not significant

b Results from a mixed model analysis of variance with year, irrigation amount, Irrigation frequency and their interactions as fixed effects.

^a: Concentration expressed as mg/L ^b: Concentration expressed as peak area. ^c:vitispirane and TDN estimated on the basis of β -damascenone

Table 3.7b Composition of volatile compounds in Syrah wines with vineyard water management from 2015 to 2016 (ug/L)

Year ^a	2015				2016				
	Irrigation mount	70/35	70/70	35/70	35/35	70/35	70/70	35/70	35/35
<i>Esters</i>									
	methyl anthranilate	2.30±1.53	1.89±0.34	1.73±0.29	1.56±0.15	0.87±0.38	0.78±0.39	1.07±1.01	0.50±0.42
	ethyl anthranilate	0.55±0.15	0.54±0.38	0.59±0.27	0.39±0.15	2.25±0.83	3.75±1.86	3.33±2.00	1.37±0.89
	ethyl phenyl acetate	3.18±1.13 ab	3.65±1.35 a	1.93±0.48 b	1.90±0.51 b	1.93±0.68	2.10±0.41	1.72±0.59	1.28±0.38
	phenyl ethyl acetate	34.8±20.3 ab	57.3±25.7 a	25.9±4.3 b	27.4±5.4 b	56.4±21.7 a	56.5±8.7 a	42.0±6.9 ab	33.9±3.5 b
<i>Terpenoids</i>									
	geraniol	18.1±2.7 b	19.7±3.5 ab	22.9±1.3 b	23.1±2.7 b	8.6±2.2 b	8.7±1.6 b	14.9±4.0 a	10.5±2.7 ab
	β-citronellol	29.1±5.6	23.8±3.2	26.9±2.1	28.7±5.4	33.5±4.5 a	36.2±4.3 a	37.5±7.2 a	24.5±5.0 b
<i>C₁₃-Norisoprenoids</i>									
	β-ionone	0.2 ± 0.03	0.19 ± 0.02	0.18 ± 0.02	0.2 ± 0.02	0.23 ± 0.07 b	0.22 ± 0.08 b	0.34 ± 0.02 a	0.2 ± 0.07 b
	TDN	7.7 ± 0.56	7.62 ± 0.69	6.75 ± 0.6	6.83 ± 0.39	7.19 ± 0.82	7.34 ± 1.05	7.05 ± 0.56	6.9 ± 0.52
<i>Alcohols</i>									
	Benzyl alcohol	188±21 a	147±31 b	172±19 ab	180±22 ab	262±39	236±29	276±18	244±31
	Propanol ^a	28.8±5.7 ab	25.0±5.7 b	34.5±3.5 a	35.6±4.7 a	30.7±8.6 bc	28.5±7.6 c	49.9±11.8 a	45.4±9.4 ab
	Methionol	1073±875 a	2506±798 b	613±417 b	402±325 b	5070±1832 b	5311±1468 b	6301±1223 ab	8571±1954 a
<i>Volatile phenolic compounds</i>									
	4-vinyl guaiacol	8.6±1.4	10.0±5.6	11.8±2.7	12.3±1.9	8.7±2.0	10.4±4.1	7.5±7.4	4.5±1.4

a Means within columns among irrigation rows within each year followed by different letters differ significantly at $p \leq 0.05$ by Tukey HSD t test. ^a: Concentration expressed as mg/L ^c: vitispirane and TDN estimated on the basis of β-damascenone

Table 3.8 Hydrolytically released C₁₃-norisoprenoids in Malbec wines produced from different treatments (µg/L)

Irrigation Amount	Irrigation Frequency	trans-β-damascenone		β-ionone		vitispirane		TDN	
		2015	2016	2015	2016	2015	2016	2015	2016
70/35	1x	29.6 ± 3.4	50.2 ± 5.3 b	0.17 ± 0.04	0.3 ± 0.15	64.2 ± 8.8	65 ± 6.8	105 ± 22	168 ± 21 b
	3x	29.7 ± 3.8	52.1 ± 3.0 ab	0.14 ± 0.05	0.43 ± 0.09	69.9 ± 9.4	60.4 ± 10.3	124 ± 25	160 ± 29 ab
70/70	1x	32.6 ± 3.1	53.4 ± 6.7 b	0.17 ± 0.03	0.36 ± 0.14	72.6 ± 8.5	86.7 ± 11.8	116 ± 28	279 ± 34 a
	3x	29.4 ± 1.1	55.7 ± 5.2 ab	0.15 ± 0.03	0.5 ± 0.12	74.7 ± 14.3	90.2 ± 18.5	119 ± 15	295 ± 52 a
35/70	1x	28.2 ± 6.1	64.7 ± 4.2 a	0.09 ± 0.08	0.53 ± 0.13	67.5 ± 17.1	80.2 ± 7	100 ± 32	237 ± 17 ab
	3x	29.8 ± 5.7	55.1 ± 1.9 ab	0.15 ± 0.04	0.52 ± 0.07	70.3 ± 21	79.3 ± 2.2	104 ± 32	220 ± 9 ab
35/35	1x	27.1 ± 2.5	52.2 ± 1.0 b	0.15 ± 0.03	0.37 ± 0.15	71.6 ± 11	91.3 ± 7.2	95 ± 7	290 ± 58 ab
	3x	28.9 ± 0.4	55.4 ± 5.3 ab	0.2 ± 0.04	0.38 ± 0.1	63.7 ± 6.8	86.8 ± 13	76 ± 19	289 ± 47 ab

Mean ± SD presented. Different letters represent significantly (Tukey HSD, P < 0.05) different in means (n = 3 independent field samples).

Table 3.9 Hydrolytically released C₁₃-norisoprenoids in Syrah wines produced from different treatments (µg/L)

Irrigation Amount	Irrigation Frequency	trans-β-damascenone		β-ionone		vitispirane		TDN	
		2015	2016	2015	2016	2015	2016	2015	2016
70/35	1x	27 ± 6.5	47.6 ± 5.6	0.16 ± 0.04	0.31 ± 0.11	183 ± 50	201 ± 35	194 ± 69	555 ± 102
	3x	28.2 ± 6.5	50.5 ± 2.4	0.2 ± 0.02	0.3 ± 0.06	132 ± 27	246 ± 26	150 ± 38	710 ± 87
70/70	1x	28.7 ± 4.2	45.6 ± 5.8	0.19 ± 0.04	0.25 ± 0.06	155 ± 14	215 ± 16	190 ± 18	489 ± 69
	3x	29.7 ± 0.9	46.2 ± 3.6	0.19 ± 0.01	0.32 ± 0.11	155 ± 22	234 ± 26	180 ± 46	589 ± 38
35/70	1x	30.1 ± 1.9	49.1 ± 3.1	0.18 ± 0.01	0.37 ± 0.12	178 ± 18	246 ± 138	221 ± 41	761 ± 406
	3x	30 ± 7.1	46.5 ± 2	0.21 ± 0.03	0.39 ± 0.08	178 ± 4	249 ± 81	229 ± 18	733 ± 332
35/35	1x	31.8 ± 2.5	47.1 ± 8.4	0.2 ± 0.02	0.27 ± 0.08	179 ± 17	213 ± 40	235 ± 18	648 ± 109
	3x	31.7 ± 8.5	47.9 ± 6.4	0.2 ± 0.01	0.26 ± 0.11	178 ± 28	257 ± 86	230 ± 27	786 ± 294

Mean ± SD presented. Different letters represent significantly (Tukey HSD, P < 0.05) different in means (n = 3 independent field samples)

Table 3.10 Odor Activity value (OAVs) for volatile compounds in Malbec wine with different irrigation treatments in 2015 and 2016

Compound	Sensory threshold ($\mu\text{g/L}$)	2015 Year				2016 Year			
		70/35	70/70	35/30	35/35	70/35	70/70	35/30	35/35
<i>Herbaceous</i>									
hexanol	8000 [2]	0.1	0.07	0.07	0.12	0.29	0.24	0.27	0.19
<i>Floral</i>									
linalool	25 [1]	0.31	0.31	0.29	0.31	1.03	0.43	0.3	0.21
α -terpineol	250 [1]	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01
β -citronellol	100 [1]	0.23	0.24	0.2	0.25	0.35	0.27	0.35	0.23
geraniol	30 [1]	0.52	0.52	0.58	0.58	0.27	0.45	0.89	0.64
nerol	290 [1]	0.02	0.02	0.02	0.02	0.04	0.03	0.02	0.02
Phenylethyl alcohol	14000 [1]	2.06	2.23	1.7	1.76	2.76	3.4	2.46	1.79
phenethyl acetate	250 [3]	0.15	0.15	0.11	0.12	0.16	0.2	0.18	0.11
<i>Berry Fruity</i>									
β -damascenone	0.02 [3]	182	178	177	176	351	310	263	223
β -ionone	0.07 [1]	3.76	2.95	2.29	3.36	6.55	5.76	8.77	5.13
<i>Phenolic (smoky, woody, roasted)</i>									
guaiacol	9.5 [8]	0.6	0.52	0.46	0.64	0.65	0.68	0.87	0.81
eugenol	6 [8]	0.18	0.17	0.15	0.16	0.41	0.23	0.4	0.32
4-vinyl guaiacol	1100 [1]	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.04
<i>Fermented (chemical, fatty)</i>									
propanol	50000 [2]	0.58	0.47	0.66	0.63	0.62	0.4	0.67	0.78
isobutyl alcohol	40000 [3]	0.74	0.85	0.77	0.68	0.54	0.75	0.53	0.46
isoamyl alcohol	30000 [3]	7.32	7.3	6.93	6.55	8.22	10.82	7.68	7.13
benzyl alcohol	200000 [4]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
hexanoic acid	420 [1]	1.2	1.21	1.27	1.36	2.62	1.99	2.48	1.69
octanoic acid	500 [1]	2.2	2.31	2.44	2.5	3.39	2.48	3.23	2.04
decanoic acid	1000 [1]	0.2	0.2	0.22	0.21	0.27	0.17	0.25	0.15
<i>Fruity</i>									
ethyl acetate	12264 [3]	2.07	1.93	2.27	2.45	5.12	3.89	5.64	6.54
ethyl butyrate	20 [1]	6.52	5.41	5.18	7.24	6.14	5.36	8.34	6.15

(Table 3.10 continued)

ethyl hexanoate	14 [1]	23.6	19.2	17.9	23.0	31.5	24.1	32.2	20.2
ethyl octanoate	5 [1]	46.5	38.5	37.3	42.0	47.4	38.2	47.7	26.8
ethyl decanoate	200 [1]	0.46	0.42	0.48	0.47	0.68	0.46	0.57	0.34
hexyl acetate	1500 [5]	0.01	0.01	0.01	<0.01	0.01	0.01	0.01	<0.01
ethyl phenylacetate	73 [6]	0.06	0.05	0.04	0.04	0.03	0.06	0.04	0.02
octyl butyrate	8200 [1]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
diethyl succinate	1200 [1]	2.19	1.82	1.53	1.86	0.65	0.59	0.67	0.66
ethyl isobutyrate	15 [1]	2.73	3.01	2.39	2.99	0.79	0.98	0.95	0.69
isobutyl acetate	1605 [5]	0.02	0.02	0.02	0.02	0.01	0.01	0.02	0.01
isoamyl acetate	30 [3]	26.7	26.0	26.4	26.6	12.0	12.2	11.9	20.4

Table 3.11 Odor Activity value (OAVs) for volatile compounds in Syrah wine with different irrigation treatments in 2015 and 2016

Compound	Sensory threshold ($\mu\text{g/L}$)	2015 Year				2016 Year			
		70/35	70/70	35/30	35/35	70/35	70/70	35/30	35/35
<i>Herbaceous</i>									
hexanol	8000 [2]	0.15	0.16	0.13	0.15	0.3	0.27	0.35	0.32
<i>Floral</i>									
linalool	25 [1]	0.27	0.31	0.32	0.29	0.27	0.23	0.27	0.22
α -terpineol	250 [1]	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
β -citronellol	100 [1]	0.29	0.24	0.27	0.29	0.33	0.36	0.38	0.24
geraniol	30 [1]	0.6	0.66	0.76	0.77	0.29	0.29	0.49	0.35
nerol	290 [1]	0.02	0.01	0.02	0.02	0.01	0.01	0.01	0.01
Phenylethyl alcohol	14000 [1]	2.09	2.47	1.51	1.43	2.91	2.78	2.93	2.61
phenethyl acetate	250 [3]	0.14	0.23	0.1	0.11	0.23	0.23	0.17	0.14
<i>Berry Fruity</i>									
β -damascenone	0.02 [3]	113	169	130	130	291	248	257	285
β -ionone	0.07 [1]	3.86	3.46	3.41	3.82	4.08	4.00	6.05	3.64
<i>Phenolic (smoky, woody, roasted)</i>									
guaiacol	9.5 [8]	1.48	1.36	1.99	1.75	2.91	2.72	3.18	2.79
eugenol	6 [8]	0.16	0.15	0.16	0.16	0.29	0.32	0.34	0.21
4-vinyl guaiacol	1100 [1]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	<0.01
<i>Fermented (chemical, fatty)</i>									
propanol	50000 [2]	0.58	0.5	0.69	0.71	0.61	0.57	1.00	0.91
isobutyl alcohol	40000 [3]	0.71	0.92	0.61	0.59	0.74	0.83	0.77	0.76
isoamyl alcohol	30000 [3]	7.2	8.7	6.3	5.9	8.8	10.1	10.8	9.2
benzyl alcohol	200000 [4]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
hexanoic acid	420 [1]	1.1	1.23	1.16	1.06	2.70	2.14	3.38	3.42
octanoic acid	500 [1]	2.01	2.33	2.23	1.99	2.95	2.58	3.76	3.05
decanoic acid	1000 [1]	0.16	0.17	0.17	0.14	0.19	0.17	0.25	0.23

(Table 3.11 continued)

<i>Fruity</i>									
ethyl acetate	12264 [3]	2.68	2.4	3.22	3.36	4.62	3.78	6.93	5.36
ethyl butyrate	20 [1]	9.04	8.08	9.96	10.59	9.78	7.59	15.25	12.61
ethyl hexanoate	14 [1]	21.9	23.9	23.8	21.2	34.0	31.6	47.9	52.5
ethyl octanoate	5 [1]	37.3	41.1	34.4	32.3	52	45.4	70.2	48.0
ethyl decanoate	200 [1]	0.4	0.45	0.41	0.38	0.57	0.5	0.68	0.62
hexyl acetate	1500 [5]	<0.01	0.01	<0.01	<0.01	0.01	0.01	0.01	0.01
ethyl phenylacetate	73 [6]	0.04	0.05	0.03	0.03	0.03	0.03	0.02	0.02
octyl butyrate	8200 [1]	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
diethyl succinate	1200 [1]	1.75	1.42	1.42	1.38	0.41	0.36	0.5	0.44
ethyl isobutyrate	15 [1]	2.35	2.46	1.91	1.84	1.02	0.86	1.01	0.69
isobutyl acetate	1605 [5]	0.03	0.03	0.03	0.03	0.02	0.01	0.03	0.02
isoamyl acetate	30 [3]	53.0	54.4	48.2	50.5	17.0	16.7	24.7	15.4

Table 3.12 The Relationship between YAN level and Ester in 2015 Malbec Wines ($\mu\text{g/L}$)

Irrigation Amount	Total straight chain esters	Total branched-chained ester	Total esters	YAN
70/35	28865 \pm 5566	913 \pm 277	29778 \pm 5836	214 \pm 29
70/70	26545 \pm 4327	891 \pm 190	27435 \pm 4384	192 \pm 42
35/70	30419 \pm 3322	887 \pm 217	31306 \pm 3470	225 \pm 46
35/35	33053 \pm 5103	907 \pm 146	33960 \pm 5192	206 \pm 32
p-value	ns	ns	ns	ns

Mean \pm SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n = 3$ independent field samples).

Table 3.13 The Relationship between YAN level and Ester in 2016 Malbec Wines ($\mu\text{g/L}$)

Irrigation Amount	Total straight chain esters	Total branched-chained ester	Total esters	YAN
70/35	64605 \pm 11332 ab	424 \pm 153	65030 \pm 11365 ab	210 \pm 41 ab
70/70	49159 \pm 10806 b	427 \pm 121	49586 \pm 10899 b	142 \pm 43 b
35/70	71033 \pm 25613 ab	420 \pm 173	71453 \pm 25725 ab	242 \pm 62 ab
35/35	81658 \pm 15711 a	660 \pm 269	82319 \pm 15640 a	292 \pm 31 a
p-value	0.023	ns	0.022	<0.001

Mean \pm SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n = 3$ independent field samples).

Table 3.14 The Relationship between YAN level and Ester in 2015 Syrah Wines ($\mu\text{g/L}$)

Irrigation Amount	Total straight chain esters	Total branched-chained ester	Total esters	YAN
70/35	35771 \pm 8841 ab	1666 \pm 547	37436 \pm 8956 ab	229 \pm 45 ab
70/70	31963 \pm 6909 b	1726 \pm 332	33689 \pm 7030 b	190 \pm 30 b
35/70	42050 \pm 4572 ab	1519 \pm 72	43569 \pm 4616 ab	242 \pm 17 ab
35/35	43674 \pm 4999 a	1590 \pm 386	45263 \pm 4855 a	294 \pm 30 a
p-value	0.019	ns	0.022	<0.001

Mean \pm SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n = 3$ independent field samples).

Table 3.15 The Relationship between YAN level and Ester in 2016 Syrah Wines ($\mu\text{g/L}$)

Irrigation Amount	Total straight chain esters	Total branched-chained ester	Total esters	YAN
70/35	58240 \pm 11129 ab	588 \pm 192 ab	58828 \pm 11298	135 \pm 20 ab
70/70	47830 \pm 10715 b	539 \pm 194 b	48368 \pm 10871	113 \pm 29 b
35/70	87144 \pm 25303 a	799 \pm 270 a	87943 \pm 25530	182 \pm 29 a
35/35	67630 \pm 18304 ab	505 \pm 323 ab	68136 \pm 18593	148 \pm 24 ab
p-value	0.006	ns	0.007	0.001

Mean \pm SD presented. Different letters represent significantly (Tukey HSD, $P < 0.05$) different in means ($n = 3$ independent field samples).

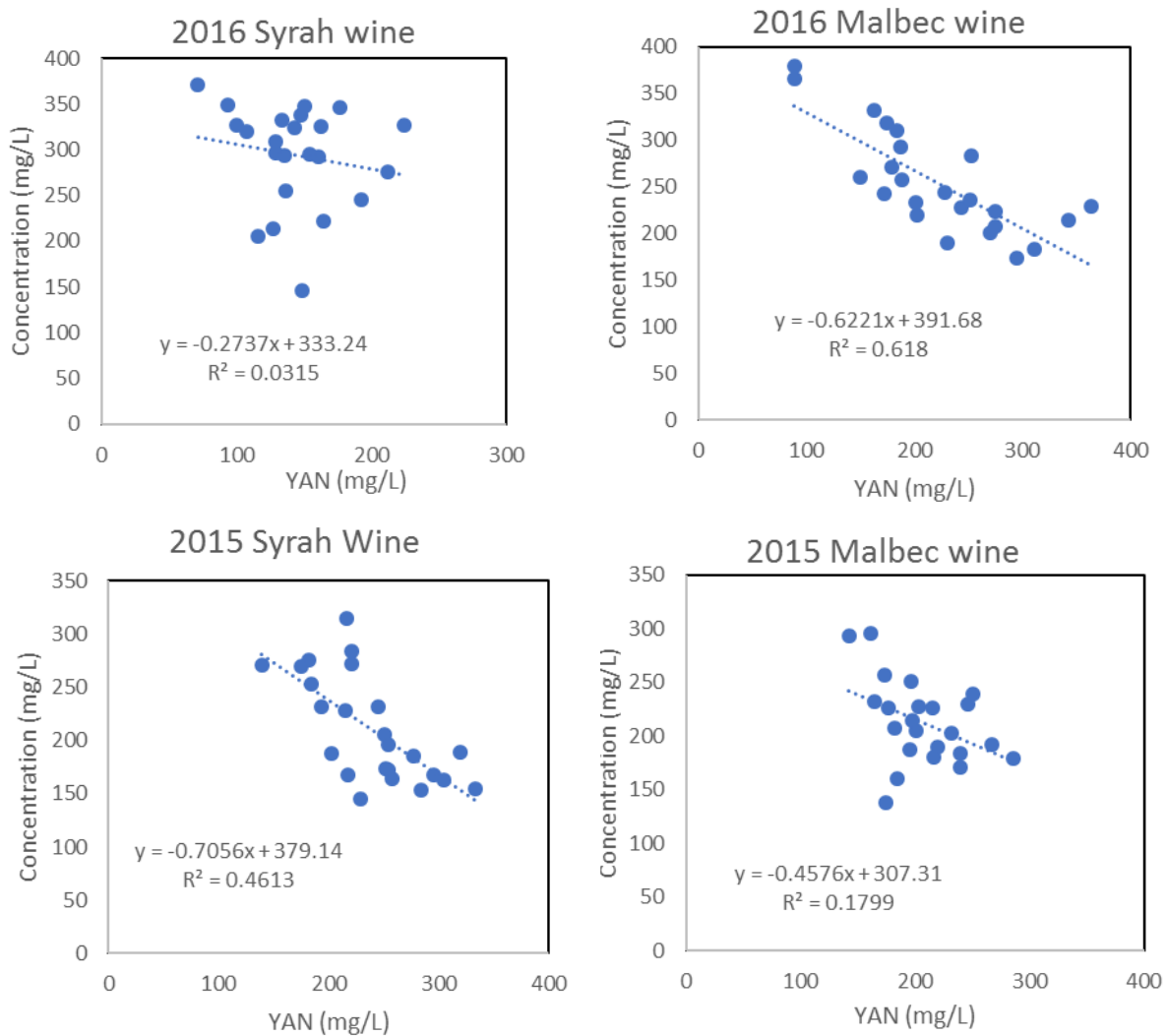


Figure 3.3 Correlation between YAN and isoamyl alcohol in the experimental wine

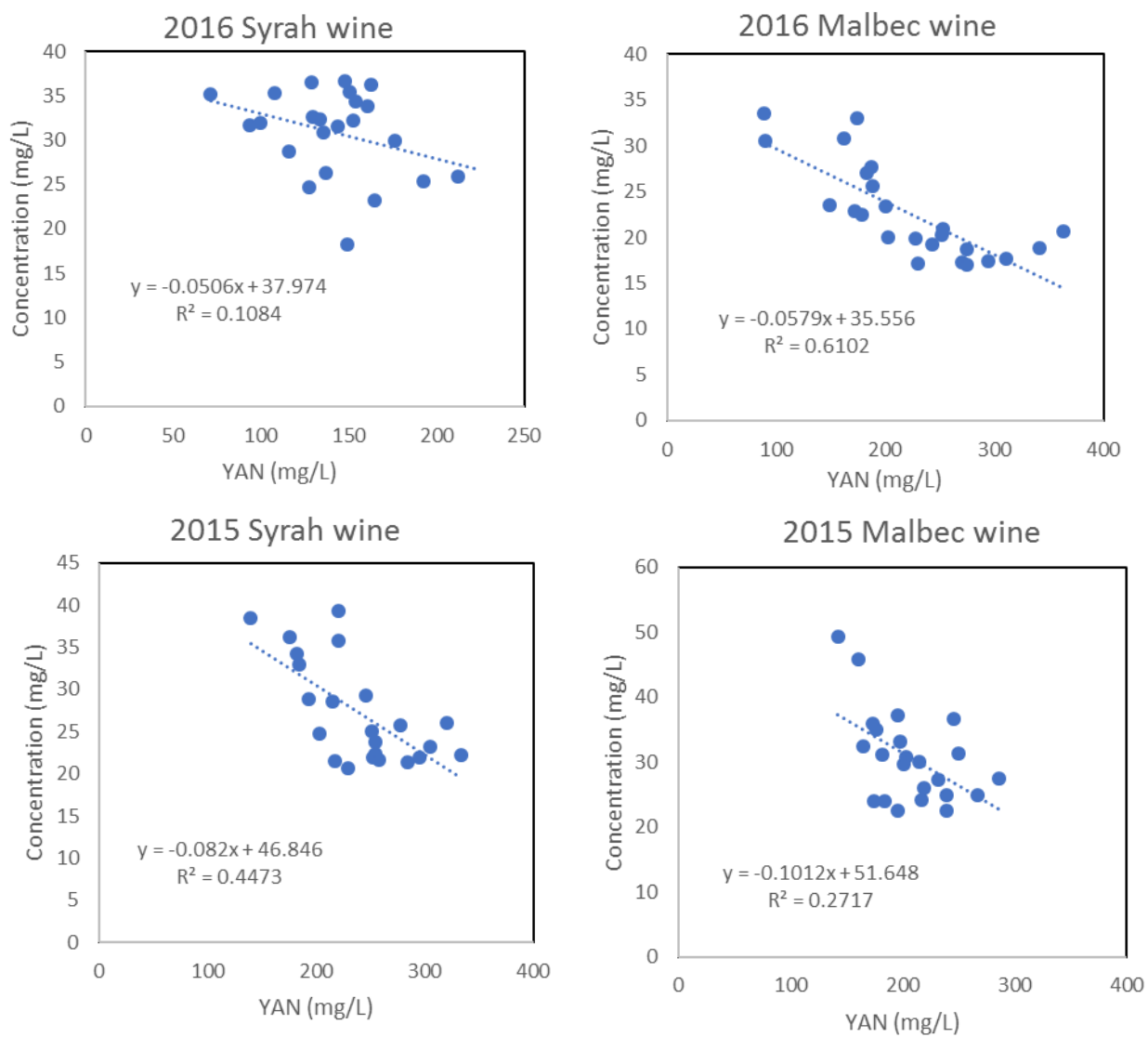


Figure 3.4 Correlation between YAN and isobutyl alcohol in the experimental wine

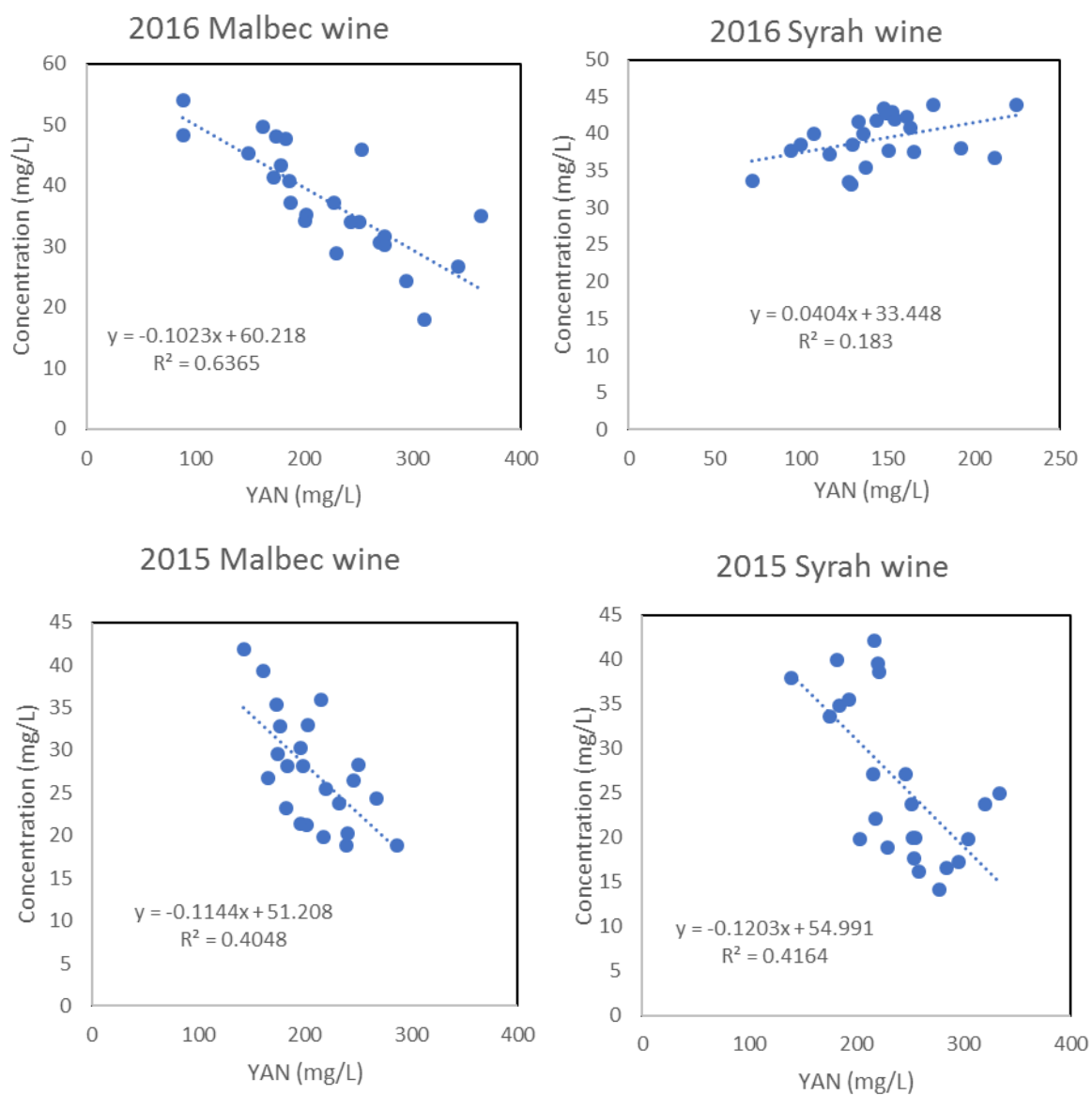


Figure 3.5 Correlation between YAN and Phenylethyl alcohol in the experimental wines

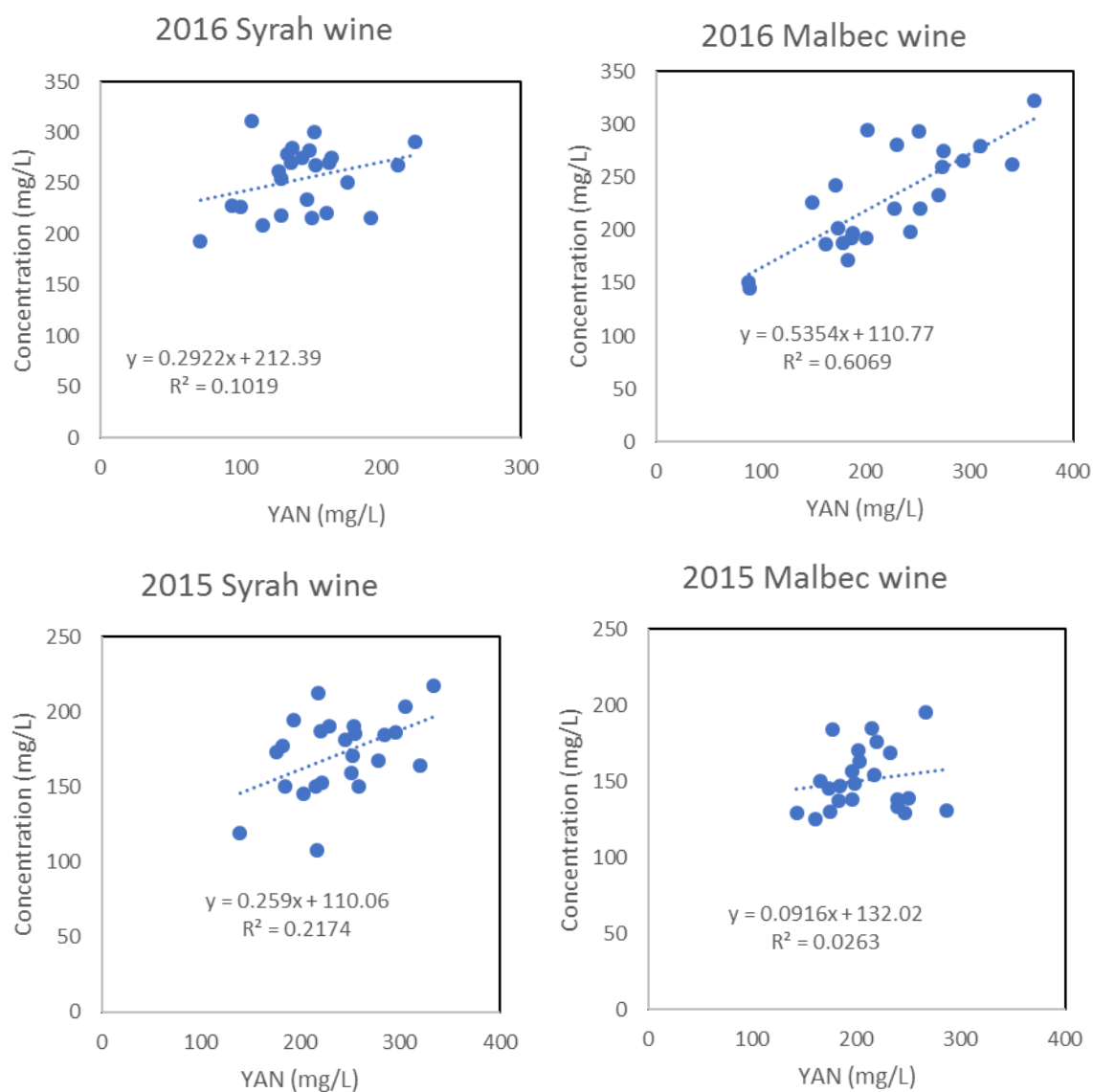


Figure 3.6 Correlation between YAN and benzyl alcohol in the experimental wines

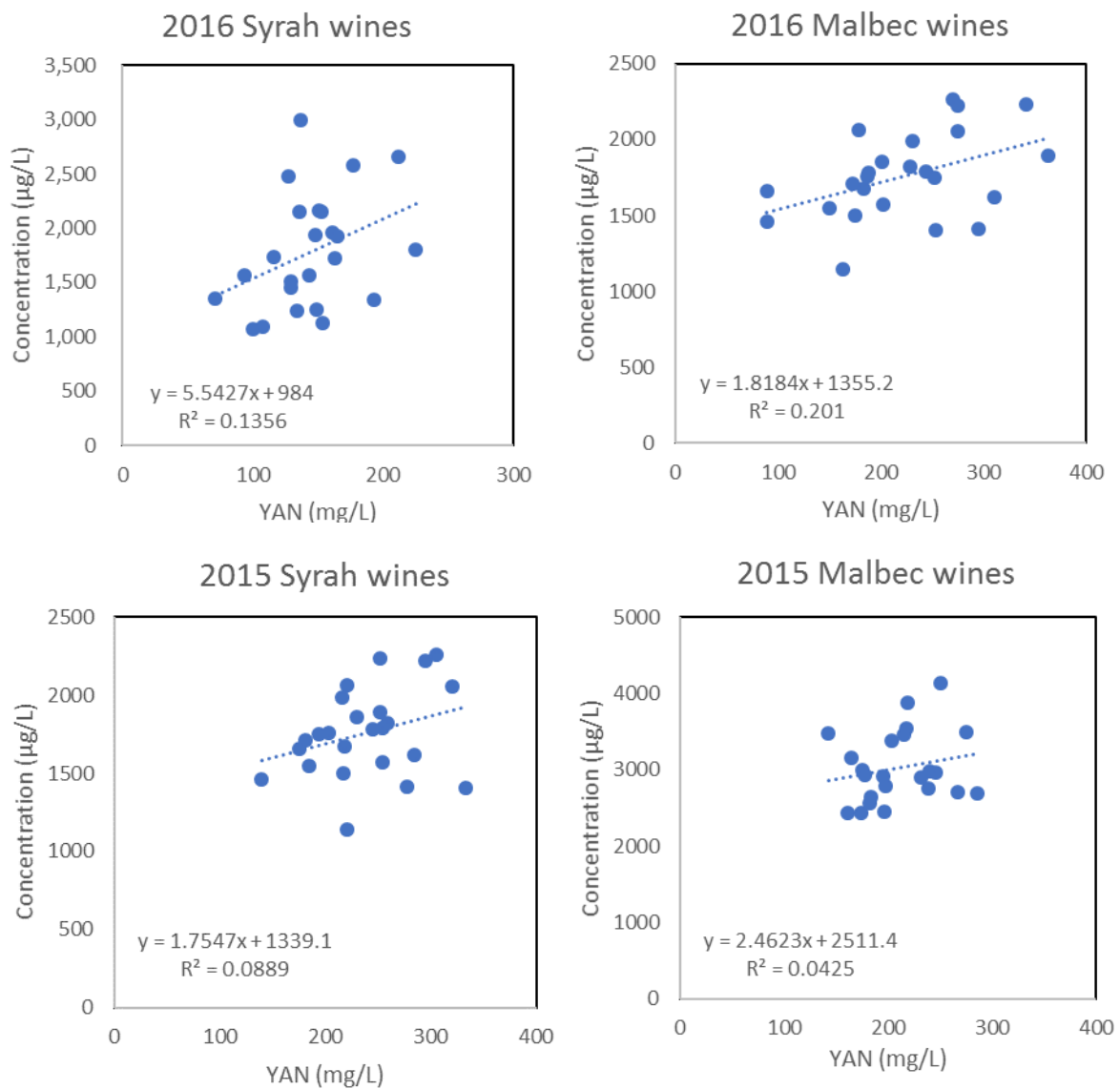


Figure 3.7 Correlation between YAN and total straight chain esters(without ethyl acetate) in the experimental wines

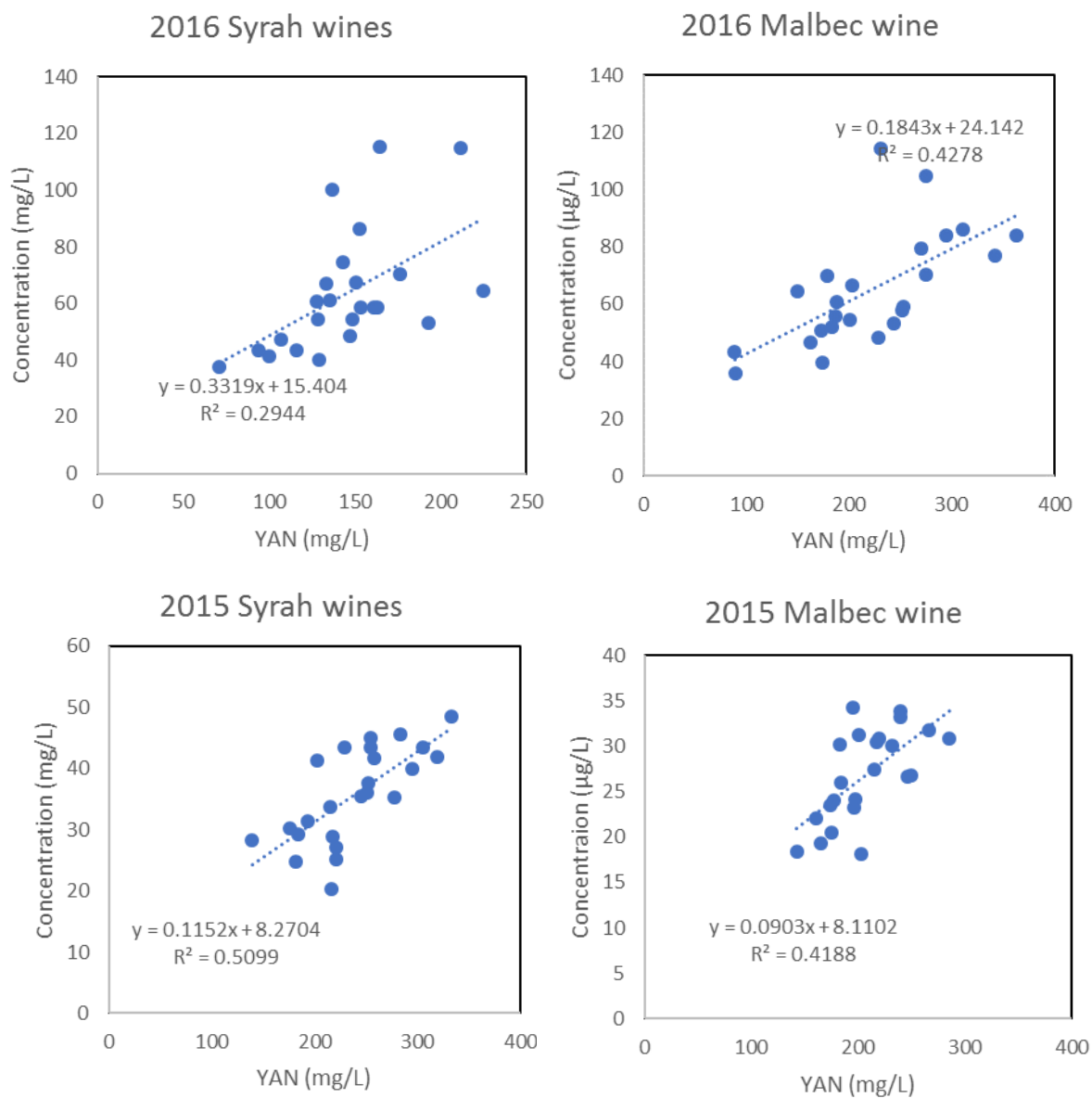


Figure 3.8 Correlation between YAN and ethyl acetate in the experimental wines

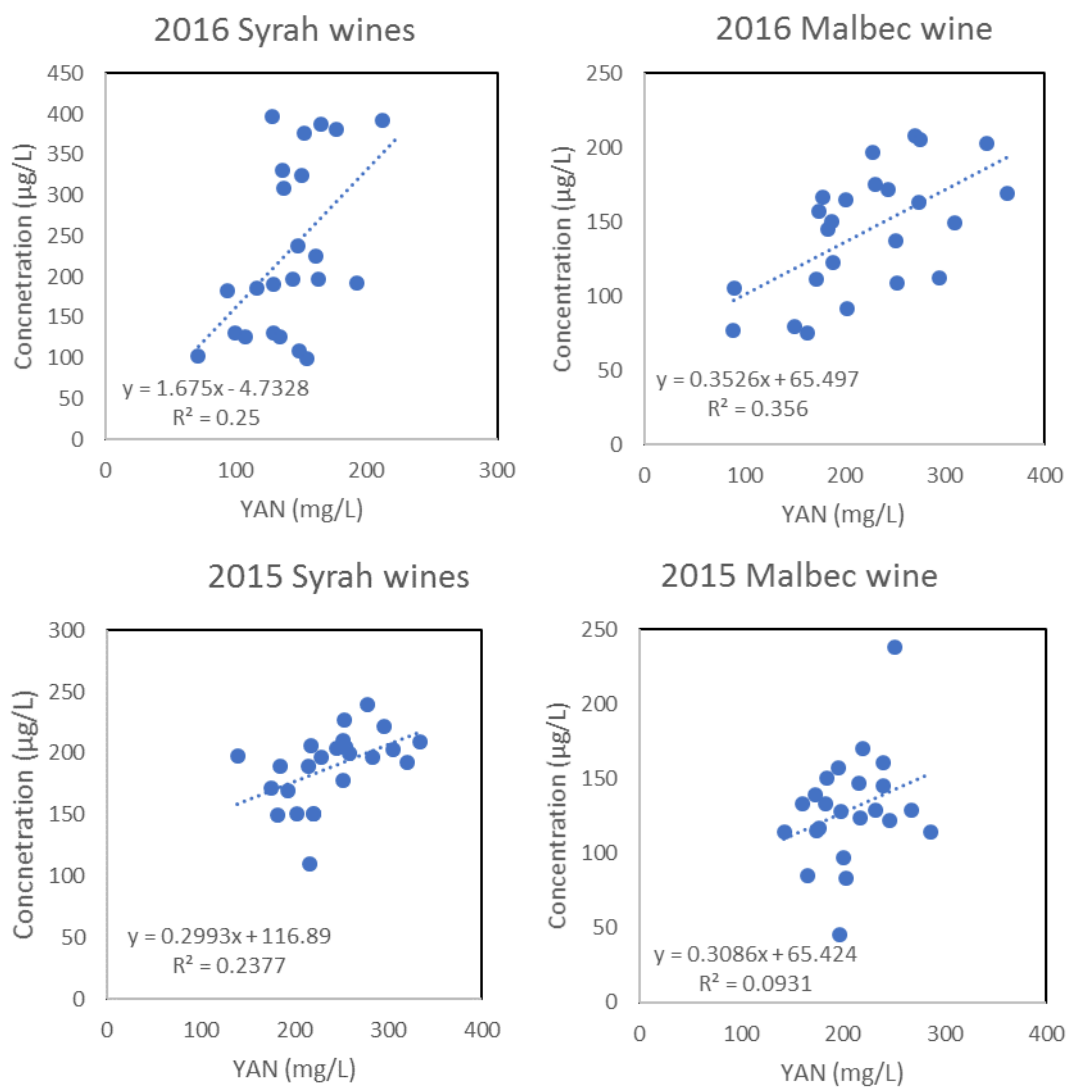


Figure 3.9 Correlation between YAN and ethyl butyrate in the experimental wines

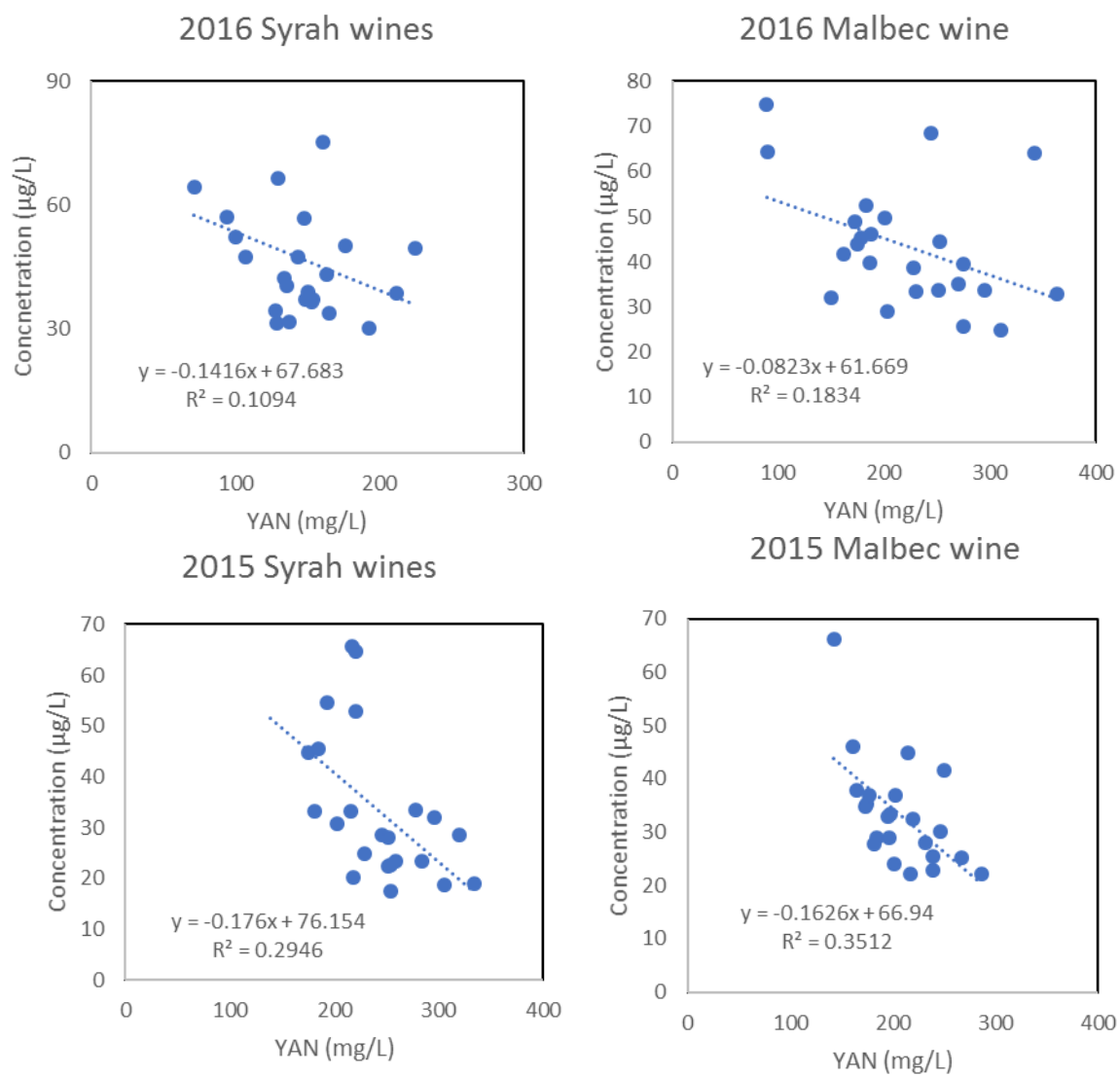


Figure 3.10 Correlation between YAN and phenyl ethyl acetate in the experimental wines

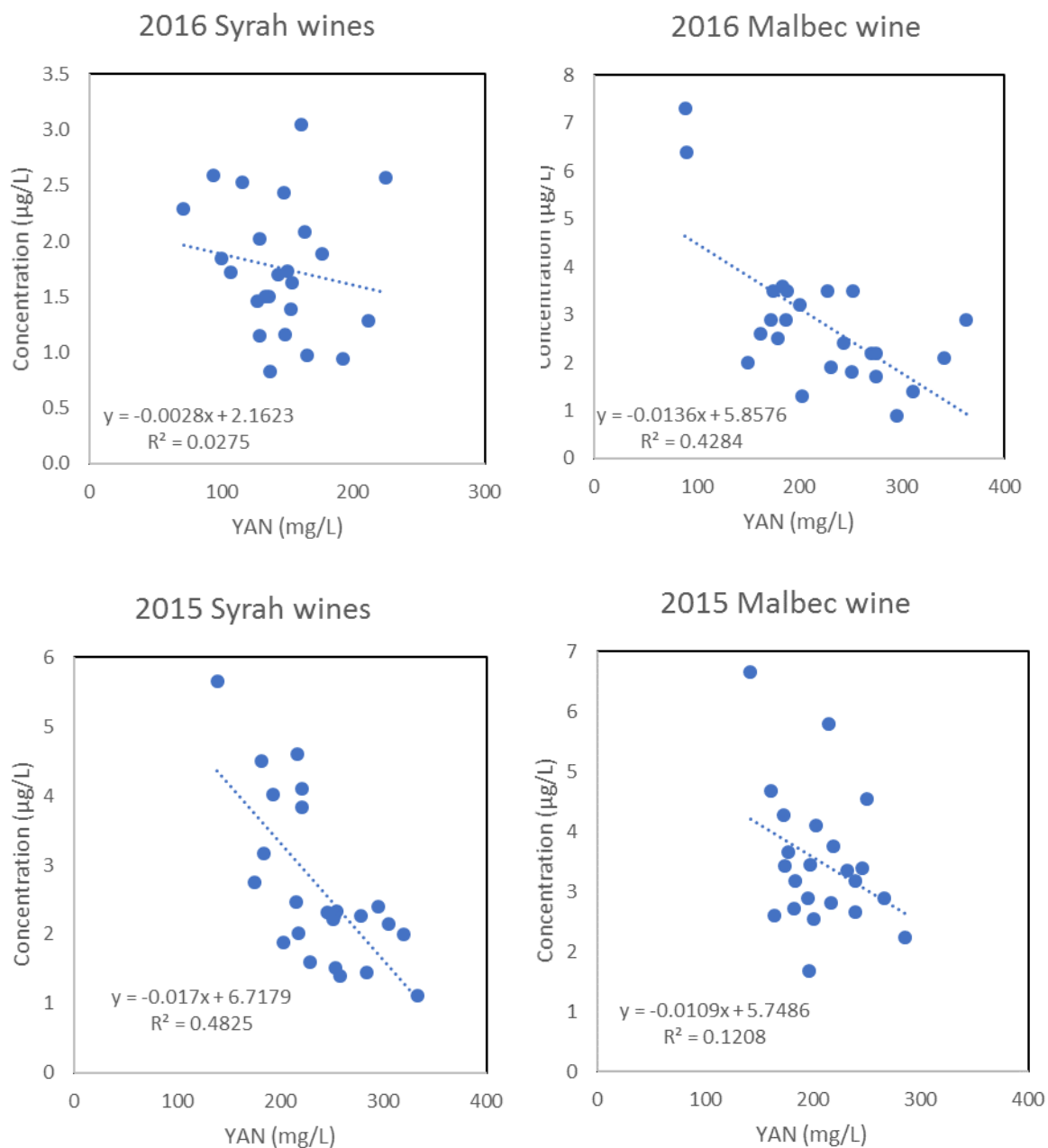


Figure 3.11 Correlation between YAN and ethyl phenyl acetate in the experimental wines

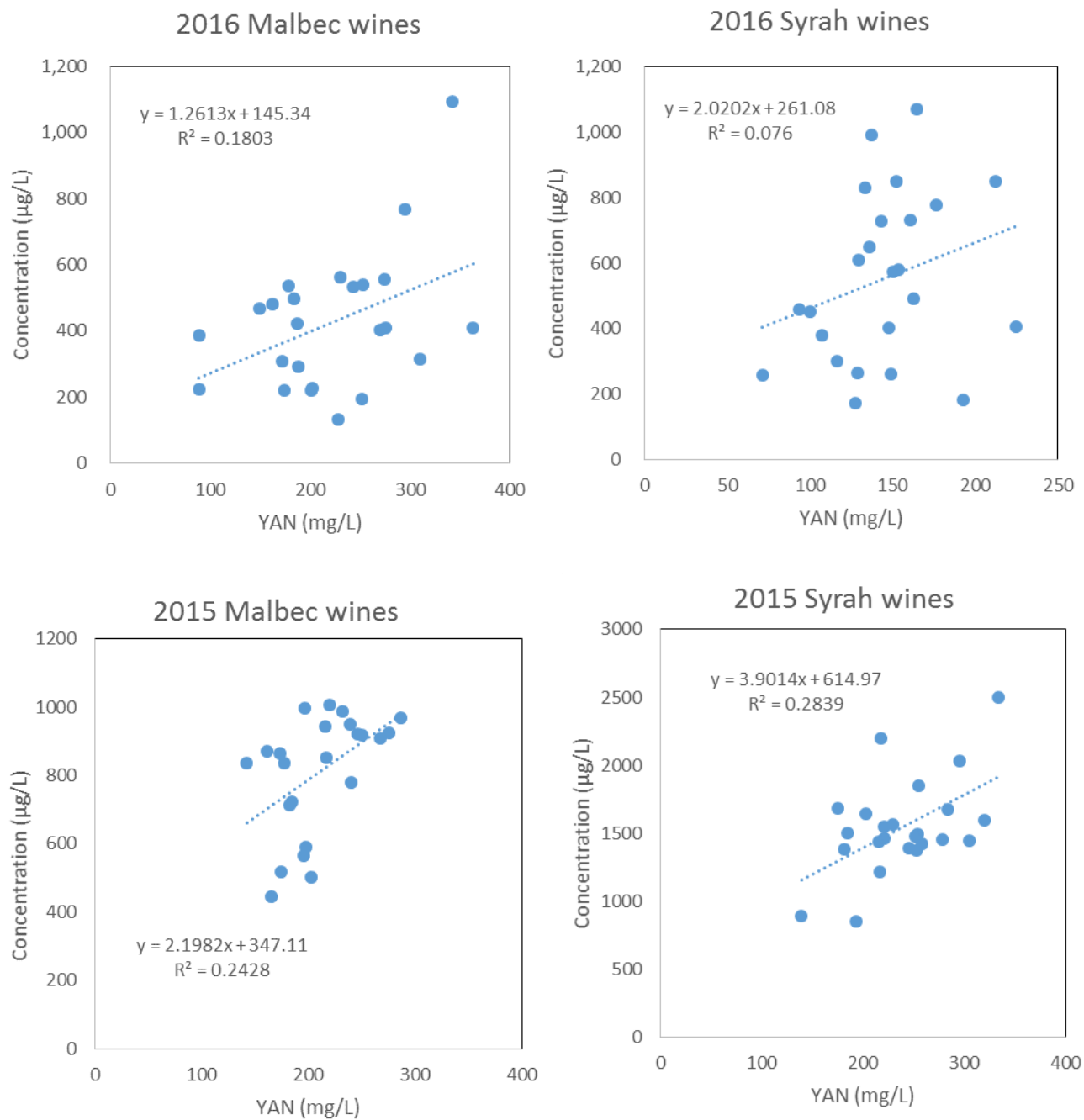


Figure 3.12 Correlation between YAN and isoamyl acetate in the experimental wines

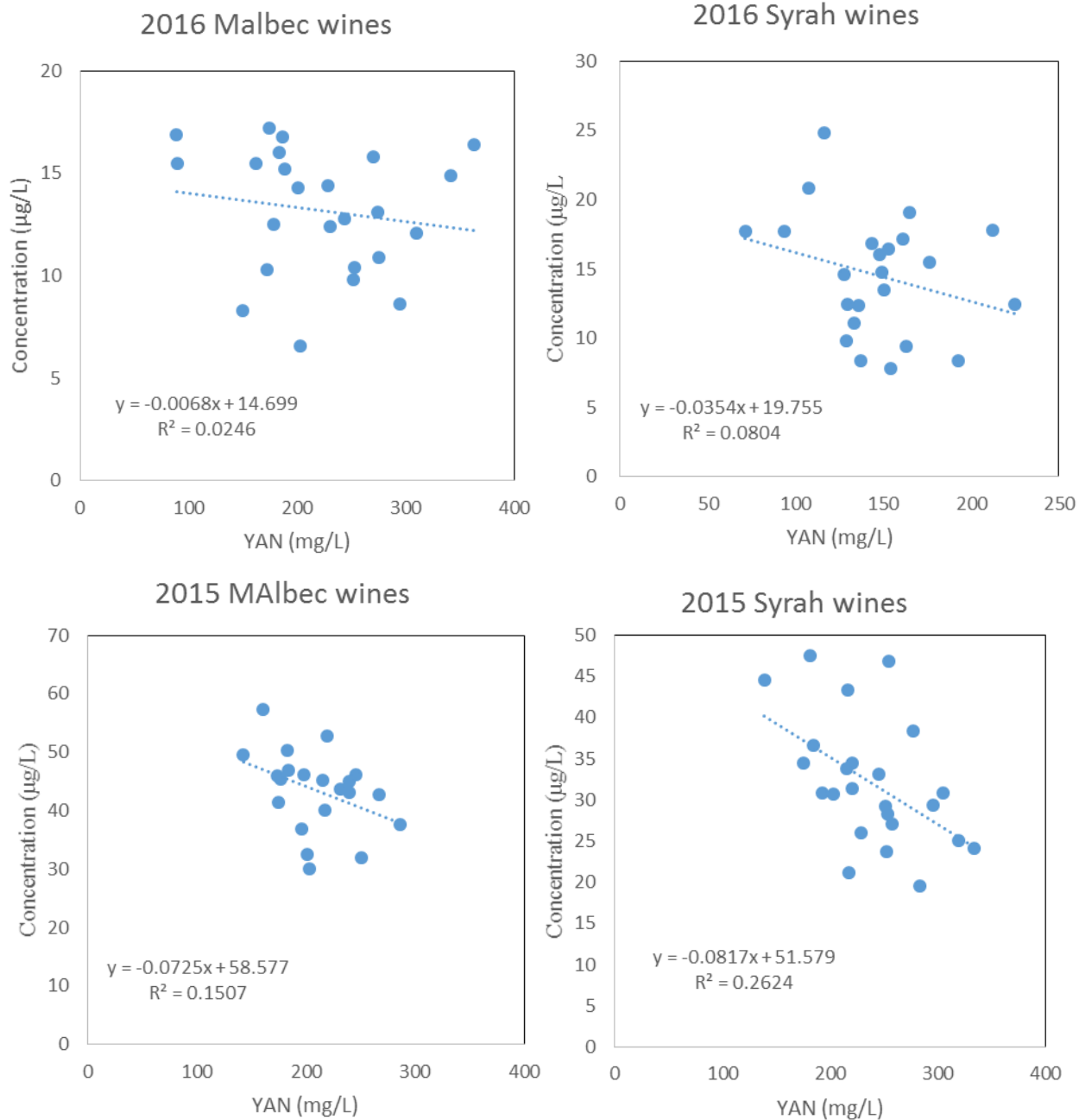


Figure 3.13 Correlation between YAN and ethyl isobutyrate in the experimental wines

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CHAPTER 4 CONCLUSION

In summary, the relationship between regulated deficit irrigation and Malbec and Syrah grape and wine volatile composition along with other quality indicators were evaluated in this research. The volatile compounds in grapes and wines were investigated by multiple techniques including HS-SPME-GC-MS, SBSE-GC-MS, HS-GC-FID and HS-SPME-GC-PFPD.

Results showed that irrigation amount showed different impacts on Malbec and Syrah grapes. Yet, irrigation frequency had less influence than irrigation amount on volatile composition in Malbec and Syrah grape berries. C₆ compounds in Syrah grapes were not influenced by different degrees of water deficit in this study. The E-2-hexenal increased with stronger water deficit. The influence of water deficit on C₁₃-norisoprenoids were variety dependent. Bound form β -damascenone, TDN and vitispirane in Malbec and Syrah grape could be affected by the time when the water deficit was supplied. In Malbec grapes, 70% ETc before veraison contributed to higher bound form β -damascenone concentration compared to 35% ETC, while 35% ETc before and after veraison all led to higher concentrations of vitispirane and TDN precursors in Syrah grapes.

The relationship between vine water status and wine composition were also studied. Total phenolic and total anthocyanins in wines were affect by irrigation amount but no obvious differences were found between two irrigation frequencies. Free form C₁₃-norisoprenoids and their precursors in wines responded differently to different irrigation treatments. Correlations were found between fermentation-derived volatile compounds and YAN level in grape must before fermentation. Isoamyl alcohol, isobutyl alcohol, Phenylethyl alcohol, ethyl isobutyrate, ethyl phenyl acetate and phenyl ethyl acetate showed negative correlations with YAN concentration, while benzyl alcohol, ethyl butyrate, ethyl acetate, isoamyl acetate and total esters increased with the increasing YAN level. In Malbec and Syrah wines, the lower YAN concentration in 70/70 irrigation amount treatment led to a higher ethyl acetate and total ester concentration, but lower

isoamyl alcohol, isobutyl alcohol, Phenylethyl alcohol, ethyl phenyl acetate and phenyl ethyl acetate concentration. The irrigation amount could alter the YAN level in grape berries, severe water deficit resulted in higher YAN concentration in both Malbec and Syrah grapes. The different water deficit degree during berry development on vine could influence the final volatile profile of the wine.

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