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Assessment fertigation effects on chemical composition of *Vitis vinifera* L. cv. Albariño

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ABSTRACT

Vineyard management can influence the growth and yield components in the vineyards and therefore on the grape and wine quality. In this work, a chemical study was conducted (2014–2015) to examine the effect of fertigation on chemical composition of Albariño. A control (Rain-fed) and fertigation (60% and 100%) treatments were apply at same irrigation depth, where fertigation 100% is complete nutrient requirements to Albariño trellis system in this location (Rias Baixas AOC, NW Spain).

Results showed that non-volatile compounds of Albariño musts were not affected by fertigation treatments. However, the effect of fertigation treatments on the volatile composition was observed. Terpenes and C_{13}-norisoprenids were the most affected families of volatile compounds by fertigation treatments, where 60% fertigation exhibited the highest concentration, improving the wine aroma quality. Application of principal component analysis (PCA) showed a good separation of Albariño grape according to fertigation treatments and vintages.

1. Introduction

Many factors, notably climate, soil, water and vineyard management, can influence the growth and yield components in the vineyards and therefore on grape and wine composition and quality.

Vineyards are subjected to a large number of management practices including row orientation, density, pruning, clipping, tilling, soil surface management or irrigation among others, which lead to changes in the microclimate of the cluster and therefore affect to grape composition (Hernandez-Orte et al., 2015; Spayd, Tarara, Mee, & Ferguson, 2002). The irrigation strategies are continuously being developed for controlling excess vigor, reducing pest and disease pressure, and optimize grape and wine quality (McCarthy, Loveys, Dry, & Stoll, 2002; Battilani & Mannini, 2000; Mirás-Avalos et al., 2017). The application of fertilisers through irrigation water is a common strategy to supply the water and nutrient requirements of grapevines (Saayman & Lambrechts, 1995; Conradie & Myburgh, 2000; Myburgh & Howell, 2012).

Nutritional factors may have an impact on variables associated with varietal typicity; however, little work has focused on the impact of vine nutrition on concentrations of aroma compounds in grapes (Reynolds & Balint, 2014). Soil nitrogen fertilization can lead to excessive vine vigor but can also enhance aroma expression. The impact of N fertilization on nitrogenous compounds in grapes is generally straighter forward than the non-nitrogenous compounds, but is not always consistent (Spayd, Wample, & Evans, 1994). Few studies have shown correlations between mineral nutrition and fruit composition, and direct connections between soil nutrients and aroma compounds have been difficult to determine. Webster, Edwards, Spayd, Peterson, and Seymour (1993) observed an increase in ‘potentially volatile terpenes’ (PVT) in grape Riesling with increased nitrogen fertilization, but there was little impact on ‘free volatile terpenes’ (FVT) except where increased vegetative growth lead to greater shading, thus decreased FVT. Vine vigor sometimes affected composition of berries, must and wines and impacted sensory perception of aroma, flavor and mouthfeel in wine, but neither variable did so consistently (Reynolds, Senchuk, & de Savigny, 2007; Reynolds & Balint, 2014). Several sensory attributes were affected by vine size. For example, high vine size decreased mineral aroma and citrus flavour and increased apple attributes (Reynolds et al., 2007). Other study has reported that nitrogen supply can increase the cysteine precursor and protective glutathione levels in Sauvignon blanc grape juice (Choné et al., 2006). Furthermore, the concentrations of volatile thiols and glutathione in wine, and the Sauvignon Blanc varietal aroma intensity of wine increased when nitrogen and sulfur were applied

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together (Lacroux et al., 2008).

Albariño is a white cultivar grown in NW of Iberian Peninsula, Galicia and north of Portugal, and its production has recently extended to other countries throughout the world. Albariño wines are characterized by a high aromatic profile with fruity and floral aroma (Versini, Orriols, & Dalla Serra, 1994). This cultivar has been the subject of several studies focused in grape and wine characterization (Carballeira Lois, Cortés Dieguéz, Gil de la Peña, & Fernández Gomez, 2001; Diéguez, Lois, Gómez, & de la Peña, 2003; Falqué, Darriet, Fernández, & Dubourdieu, 2008; Oliveira, Oliveira, Baumes, & Maia, 2008; Vilanova & Sieiro, 2006; Vilanova, Genisheva, Masa, & Oliveira, 2010). The effect of ammonium nitrogen supplementation of grape juice on wine volatiles and non-volatiles composition of the aromatic grape variety Albariño also was studied by Vilanova, Varela, Siebert, Pretorius, and Henschke (2012). However, no studies have been conducted on the fertigation effect on volatile profile of Albariño musts, despite the importance of volatiles on white grape and wine aroma. With the aim of addressing the lack of researches in this field and considering that the grape quality depends on water and nutrients among others, the present work aimed at evaluating the detailed composition of the grape volatiles as response to different fertigation treatment. Then, fertigation 60% (F-60) and 100% (F-100) compared with a control, were apply with the aim to know the combined effect of water application and nutrient on grape quality. The study was carried out on *Vitis vinifera* L. cv. Albariño during 2014–2015 seasons to evaluate the effect of fertigation treatments on must volatiles in free and glicosidically bound fractions and no-volatile composition.

2. Material and methods

2.1. Experimental conditions

The experiment was carried out over two years (2014 – 2015), in a commercial *Vitis vinifera* Albariño vineyard planted in 1996 on 110-Richter at a spacing of 3 × 2 m (1667 vines/ha). The vineyard was located in wine-growing sub-region of O Rosal (Rías Baixas AOC, Pontevedra, NW Spain) (Latitude: 41.94507, Length: −8.82520, 37 m.a.s.l.). Vines were trained to a vertical trellis system on a Guyot oriented in the East–West direction. The soil at this site presented a sandy-loam texture (66.1% sand, 18.5% silt and 15.4% clay), slightly acid [pH (H_2O) = 6.2] and with a high organic matter content (7.8%). Soil depth varied with the slope of the plot, in average it was deeper than 1.2 m.

Agrometeorological data were obtained from a nearby station 'O Rosal' maintained by the Consellería de Medio Rural, Xunta de Galicia (Latitude: 41.93873, Length: −8.78974, WGS84, 47 m.a.s.l.). Precipitation (P) and reference evapotranspiration (ET_o) for the period from March to October in 2014–2015 are shown in Fig. S1.

2.2. Experimental design and fertigation treatments

The experimental study included two fertigation treatments: fertigation 60% (F-60) and 100% (F-100) were apply at same irrigation depth, where fertigation 100% is complete nutrient requirements to Albariño trellis system in this location. The amount of nutrients applied to the vineyard each year has been determined from foliar and soil analyzes, carried out in the trial plot, each year. The fertilizer units are applied by each stage of development stage of the vineyard, to reach the maximum productive established by the Denomination of Origin, of 12000 kg/ha. The irrigation treatments were compared with a control, without irrigation and nutrients, Rain-fed (F-0). The irrigation system applied was surface drip irrigation, with pressure-compensating drip of 2 l/h per emitter, from driplines located 30 cm above the ground, and separated 0.75 cm between emitters.

Both the F-60 and F-100 systems were also used to apply nutrients N, P, K, Mg and Ca (Table 1), these applications were scheduled for 45 min daily on average, six days per week from mid-July to first days in September in 2014 (66 mm in total), and from end-April to end-August of in 2015 (65 mm in total). The irrigation dose applied is that established and typically used by vine growers at the surrounding commercial vineyards in the study region. The treatments were carried out in triplicate and were arranged in a proportional stratified sampling design with 7 vines for each replication.

Table 1
Fertilizer units applied during the fertigation seasons. F-60: Fertigation 60%; F-100: Fertigation 100%;F-0: Rain-fed.

Treatment	2014			2015		
	F-0	F-60	F-100	F-0	F-60	F-100
N	0	26.4	44.1	0	42.4	70.6
P2O5	0	8.6	14.4	0	12.1	20.2
K2O4	0	21.7	36.2	0	44.6	74.4
MgO	0	4.1	6.8	0	9.0	14.9
Ca	0	0	0	0	12.4	20.7

2.3. Grape samples

Grape samples (1 Kg) for replication from white Albariño cultivar were harvested at their optimum maturity (18–20 °Brix, a common harvesting criterion for this variety in this area, was established by the winery) during two consecutive seasons 2014 (September 25th) and 2015 (September 14th). Samples were destemmed and crushed to obtain the must by Thermomix (Worwerk, Germany) at speed 4 during 20 s to ensure the same pressing on all samples. The enological parameters were immediately determined in the obtained musts. Then must samples of 300 mL were frozen and stored at −20 °C in order to determination of volatile composition.

2.4. Enological parameters

Musts were physicochemical analyzed by determination of sugar content (glucose and fructose), malic and tartaric acid, Free amino N (FAN), Ammonia and Yeast assimilable N (YAN) and IPT, by using a Foss WineScan FT 120, as described by the manufacturer (Foss, Hillerød, Denmark). All determinations per replication were performed in triplicate. Grape samples of 300 g were used to analyze volatile composition of *Albariño* musts.

2.5. Analysis of volatile compounds by GC–MS

In order to carry out the extraction of volatile compounds the method described by to Oliveira et al. (2008) was used with some modifications. About 300 mL of Albariño must was centrifuged (*RCF* = 9660, 20 min, 4 °C) and filtered through a glass wool bed. To 75 mL of juice, 3 μg of 4-nonanol (Merck, ref. 818773) were added and passed through a LiChrolut EN cartridge (Merck, 500 mg, 40–120 μm). The resin was previously pre-conditioned with 10 mL of dichloromethane, 5 mL of methanol and 10 mL of aqueous alcoholic solution (10%, v/v). Free and bound fractions were eluted successively with 5 mL of pentane–dichloromethane azeotrope and 7 mL of ethyl acetate, respectively. The pentane–dichloromethane elute was dried over anhydrous sodium sulphate and concentrated to 200 μL by solvent evaporation with N prior to analysis. The ethyl acetate eluate was concentrated to dryness in a Multivapor™ from Buchi (40 °C) and redissolved in 200 μL of 0.1 M citrate–phosphate buffer (pH = 5.0). Fourteen milligrams of enzyme Rapidase Revel aroma (Erbslöh, Germany) were added to the glycoside extract and the mixture was incubated at 40 °C, for 12 h. Released aglycons were extracted with pentane-dichloromethane azeotrope, after addition of 3 μg of 4-nonanol as internal standard. The organic phase was then concentrated to

200 μL with N.

Gas chromatographic analysis of volatile compounds was performed using an Agilent GC 6890 N Chromatograph coupled to mass spectrometer Agilent 5975C. A 1 μL injection was made into a capillary column, coated with CP-Wax 52 CB (50 m × 0.25 mm i.d., 0.2 μm film thickness, Chrompack). The temperature of the injector was programmed from 20 °C to 250 °C, at 180 °C/min. The oven temperature was held at 40 °C, for 5 min, then programmed to rise from 40 °C to 250 °C, at 3 °C/min, then held 20 min at 250 °C and finally programmed to go from 250 °C to 255 °C at 1 °C/min. The carrier gas was helium N60 (Air Liquide) at 103 kPa, which corresponds to a linear speed of 180 cm/s at 150 °C. The detector was set to electronic impact mode (70 eV), with an acquisition range from 29 to 360 m/z, and an acquisition rate of 610 ms.

Identification was performed using the GC/MSD ChemStation Software (Agilent), by comparing mass spectra (Wiley and Nist libraries) and retention indices with those of pure standard compounds. Pure standard compounds were purchased from Sigma-Aldrich (Darmstadt, Germany) with purity higher than 98%. All of the compounds were quantified as 4-nonanol equivalents.

2.6. Statistical analysis

All chemical data are presented as means from replicate determinations and treatments and processed with Microsoft Excel 2016. A two-way variance analysis (ANOVA) was used for to evaluate the differences among treatments, vintages and interaction TR*Y. Tukey's multiple comparation test ($p < 0.05$) was applied to determine differences between samples by vintage. Principal Component Analysis (PCA) was used on volatile composition (free and bound fractions) by families of compounds to discriminate treatments and vintages. All data were analysed using statistical package XLSTAT-Pro 2017 (Addinsoft, Paris, France).

3. Results and discussion

3.1. Weather conditions

The climatic conditions (precipitation and ET_o) during the growing season from 2014 and 2015 seasons are shown in Fig. S1. In the period, from March 1 to harvest, 830 mm of precipitation accumulated in 2014, compared to 389 mm in 2015. From mid-April to the end of August, rainfall was scarce in 2015, while in the year 2014, rainfall occurred continuously throughout the vineyard cycle. This fact has generated a higher reference evapotranspiration (ET_o) in 2015, with values higher than 6 mm per day, although the total accumulated in both years is similar, around 645 mm. These climatic differences between seasons, had affected to enological parameters, and to aroma compounds pattern, as showed in next sub-sections. Cancela et al. (2016) achieved similar results in relation to precipitation and ET_o patterns, to several white varieties in Galicia, including Albariño, where special attention should be taking into account to irrigation management, in situations with water scarce and/or irregular precipitation patterns.

3.2. Effect of fertigation on enological parameters of Albariño musts

Table 2 shows the changes produced in the standard chemical parameters analyzed in Albariño musts when irrigation treatments F-60, F-100 and Control (F-0) were applied. Fertigation treatment not affected significantly the physicochemical parameter studied in none of the years of study. The ANOVA results shown no significant differences among treatments, years and neither interaction Treatment*Year was observed. However, an increasing trend was observed for sugar content (glucose and fructose) when fertigation treatments were applied (F-60 in 2015 and F-100 in 2014) versus control (F-0).

The comparison of the fertigation treatments provided no relevant differences between seasons with respect to malic acid, thus the same behavior was observed increasing their concentration when fertigation was applied respect to control (F-100 in 2014 and F-60 in 2015). In contrast, tartaric acid showed a trend to increase their concentration in control samples for the two seasons, mainly in 2014.

Table 2
Enological parameters of fertigation treatments and control in two consecutive vintages (2014–2015). F-60: Fertigation 60%; F-100: Fertigation 100%; F-0: Rain-fed.

Enological Parameters	2014			2015			Sig		
	F-0	F-60	F-100	F-0	F-60	F-100	Y	Tr	Y*Tr
°Brix	20.0	18.5	18.5	17.5	17.5	19.0	ns	ns	ns
Glu + Fru	112.5	128.2	149.9	137.1	219.9	144.1	ns	ns	ns
Malic acid	5.0	7.5	9.2	5.4	11.2	6.5	ns	ns	ns
Tartaric acid	4.1	2.5	3.2	3.9	3.7	3.2	ns	ns	ns
FAN	317.5	298.0	328.5	135.5	266.5	259.5	ns	ns	ns
N Ammonia	146.5	111.0	271.5	66.0	105.0	189.5	ns	ns	ns
YAN	464	409	600	201.5	371.5	449	ns	ns	ns
IPT	0.15	0.3	0.3	0.3	0.55	0.35	ns	ns	ns

Glu + Fru: glucose + fructose; FAN: free assimilable nitrogen without proline; YAN: yeast assimilable nitrogen; IPT: total polyphenol index; Y: year; Tr: treatment; Level of significance: ns indicates no significant difference.

On the other hand, total polyphenol index showed higher values when the irrigation treatment was applied *vs* control in both years studied, however these differences was not significant.

Nitrogen is the most abundant soil-derived macronutrient in a grapevine, and plays an important role in quality components in the grape. In addition, fermentation kinetics and formation of flavor active metabolites are also affected by the nitrogen status of the must (Bell and Henscke, 2008). The nitrogen application in the vineyard induce an increase of the major nitrogenous compounds, such as total nitrogen, total amino acids, arginine, proline and ammonium, and consequently YAN in grape berry. As expected, the highest levels of YAN, ammonia and FAN, were found in fertigation samples (F-100 and F-60) in 2015. Other authors have reported increases in the must concentration of various nitrogenous compounds (ammonia and total N) with application of N fertilizer (Bell, Ough, & Kliewer, 1979; Kliewer, 1971). Garde Cerdán et al. (2015) observed that the foliar application of proline, phenylalanine and urea to Tempranillo vines not affect to any physicochemical parameters studied. However, total acidity and probable alcohol were affected when urea was applied to Merlot grapevine (Lasa et al., 2012).

3.3. Effect of fertigation on volatile composition of Albariño

Fig. 1 shows the total volatile composition (free and bound fraction) for both vintages studied (2014 and 2015). Free fraction reached the highest concentrations of total volatiles in all fertigation treatments for the both vintages studied *vs* bound fraction. However, only significant differences among treatments were observed in the free fraction for 2014 vintage, where F-60 reached the highest value *vs* control. Similar tendency was observed for 2015 season. Respect to the bound fraction, the behavior was different between years and none of the years showed significant differences among fertigation treatments. F-100 showed the tendency to increase the total volatile concentration for 2014, however the control (F-0) reached the highest level in 2015 vintage *vs* both irrigation treatments.

Tables 3 and 4 show the results of volatile composition of Albariño musts according to fertigation and control treatments in free and bound fraction, respectively.

The free fraction was represented by 39 volatile compounds (Table 3) grouped into ten chemical families (C_6-compounds, ethyl esters, phenol volatiles, carbonyl compounds, terpenes, C_{13}-norisoprenoids, alcohols, volatile acids, lactones and aldehydes). Alcohols

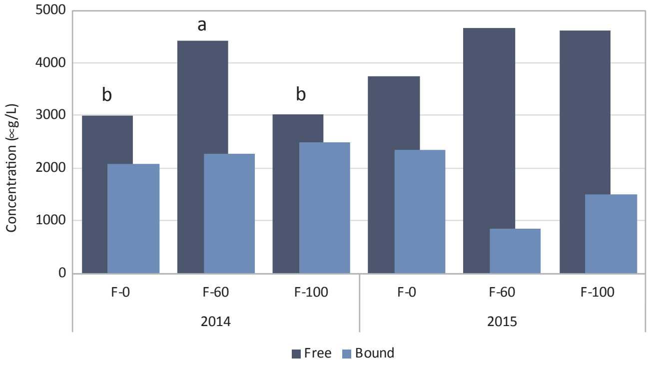

Fig. 1. Total volatile composition of Albariño grapes concentration (µg/L) from irrigation treatments and control (2014–2015): F-60: Fertigation 60%; F-100: Fertigation 100%; F-0: Rain-fed. Values with different roman letters are significantly different according to the Tukey's test ($P < 0.05$).

in 2014 and C_6-compunds in 2015 reached the highest concentration in all treatments.

When each year was considered separately, significantly differences among the treatments were observed for the 2014 season (Tukey's test for $p < 0.05$), where only 6 free compounds were modified by the treatment, increasing their concentration for F-60 respect to the control samples: 2 + 3-methyl-1-butanol and 3-methyl-1-pentanol (161% of increase with respect to the control), trans-pyran linalool oxide (169% of increase with respect to the control), 3-oxo-7,8-dihydro-a-ionol (193% of increase with respect to the control) and geranic acid (181% of increase with respect to the control). None of the treatments affected to the must free volatile composition in 2015.

The bound fraction was represented by 49 volatile compounds (Table 4) arranged into seven chemical families (C_6-compounds, ethyl esters, phenol volatiles, terpenes, alcohols, volatile acids, lactones). Bound terpenes and C_{13}-norisoprenoids and bound acids were the most abundant volatile families in all treatments, F-0, F-60 and F-100, respectively. Only bound (*E*)-3-hexenol in 2014 vintage was influenced by fertigation treatment increasing significantly its content in control samples with respect to fertigation treatments. However, the treatments not affected to the must bound composition in 2015 (Tukey's test for $p < 0.05$).

Tables 3 and 4 also show the two-way ANOVA results. A significantly stronger effect of the vintage with respect to the treatment was observed in free (nine compounds: benzyl alcohol, 2-phenylethanol, E-2-hexanol, E-2-hexenol, nerol, diendiol I, benzaldehyde, hexanoic and E-2-hexanoic acids) and bound (six compounds: benzyl alcohol, 2-phenylethanol, E-2-hexenol, Z-8-hydroxylinalool, hexanoic and E-2-hexanoic acids) fraction of volatiles. The amount and distribution of precipitation in both years, has caused a different effect of fertigation treatments, in relation to the aromatic concentrations present in the musts. The management of irrigation water and nutrients should consider these climatic patterns, when applying fertigation in AOCs with a Categorized Index defined as Temperate, humid, and with cool nights (Fraga et al., 2014). None of compounds analyzed in free and bound fraction showed the interaction treatment ∗ year (TR + Y).

Although most higher alcohols are a by-product of fermentation by yeast, some are found in the grape and are sustained through the fermentation process (e.g. 2-ethyl-1-hexanol, benzyl alcohol, 2-phenylethanol, 3-octanol and 1-octen-3-ol). The straight chain higher alcohols are considered to have the most significant sensorial impact [e.g. 1-propanol, 2-methyl-1propanol (isobutyl alcohol), 2-methyl-1-butanol and 3-methyl-1-butanol (isoamyl alcohol)] (Pretorius & Lambrechts, 2000). ANOVA showed no significant differences among treatments in free and bound alcohols. However, the vintage affected to benzyl alcohol and 2-phenylethanol in both fractions of volatiles.

In general, total free and bound alcohols showed a trend to increase their concentration when fertigation treatments were applied. Ough and Bell (1980) showed that fertigation increased the concentration of higher alcohols in Thompson Seedless wines from California. Among alcohols an increase of 2-phenylethanol was observed by Garde Cerdán et al. (2015) when nitrogen was applied to Tempranillo vines. In our study the trend to increase 2-phenylethanol in Albariño must was observed in F-60 and F-100 respect to the control samples, but only in 2014 season.

Regarding C_6-compounds group, comprises alcohols and aldehydes, which derive from membrane lipids via the lipoxygenase pathway and they are important contributors to the flavour of many fruits and vegetables (Oliveira, Faria, Sá, Barros, & Araujo, 2006; Schwab, Davidovich-Rikanati, & Lewinsohn, 2008). Our work shows that free and bound C_6-compounds were no significantly affected by the fertigation treatments, however a trend to increase in free faction for F-60 was observed. In bound fraction that trend was observed for control samples (F-0). Our results obtained in bound fraction of volatiles agreed with those found by Zalacain, Marín, Alonso, and Salinas (2007), where foliar treatment with nitrogen fertilizers decreased total C_6-compounds in relation to the control. However, none of the foliar treatment affected to C_6-compounds in Tempranillo vine (Garde Cerdán et al., 2015).

In the grape, monoterpenes, sesquiterpenes and C_{13}-norisoprenoids are present either in a free volatile form, or bound to sugars and rendered non-volatile (Black et al., 2015). Terpenoids synthesis decreased when Tempranillo vines were treated with foliar nitrogen fertilizers (Garde Cerdán et al., 2015). Respect to the C_{13}-norisoprenids not significant differences effect was observed for treated Tempranillo samples with foliar amino acids treatment (Garde Cerdán et al., 2015). In our study, two free terpenes (trans-piran linalool oxide and nerol) were significantly affected by the treatment (as mean 2014–2015). Both free terpenes showed the highest concentration for F-60. A trend to increase the total free terpenes concentration was observed when F-60 was applied. In bound fraction none of terpenes were affected by the fertigation treatments. Phosphorous and nitrogen fertigation increased the concentration of free monoterpenes and wine quality by sensory evaluation (Bravdo & Hepner, 1987). Nitrogen affects the production and quality of the berries by direct effect on proline, arginine and volatile esters in the must whereas P was reported to affect free and bound monoterpene content of must and wine (Bravdo, 2000).

Grape-derived aliphatic alcohols and aldehydes were identified as precursors to acetate esters in wine (Dennis et al., 2012). In particular, the C_6-compounds (*E*)-2-hexenal, hexanal, (*E*)-2-hexen-1-ol, and hexan-1-ol were shown to be precursors to hexyl acetate. Among esters, only bound hexyl acetate was affected by the treatment, showed lowest when fertigation was applied *vs* control (mean of two vintages) according to higher level observed in bound 1-hexanol for F-0. Other studies showed hexyl acetate and other esters quantified in Tempranillo musts were not affected by nitrogen treatments (Garde Cerdán et al., 2015). Esters play an important role in wine aroma and they are formed in high quantity as consequence of alcoholic fermentation (Jackson, 2008). In general, total ethyl esters showed a tendency to increased their concentration for control samples. According to our results Ough and Lee (1981) observed that increased vineyard fertilization could increase most esters such a isoamyl acetate Thompson Seedless as consequence of increase must amino nitrogen and resultant transamination.

3.4. Principal components analysis (ACP)

In basis to explore and visualize graphically the results about the effect of treatment on must composition by vintage, two PCA was applied on the data of volatile compounds grouped by families (Fig. 2). Despite the few significant differences among fertigation treatments, the application of PCA analysis is important to examine the results. The application of this statistical tool allowed for grouping the chemical groups of volatile compounds relating them with the irrigation

Table 3
Free volatile composition of Albariño grapes by individual compounds (μg/L) and by groups (%) from fertigation treatments and control (2014–2015). F-60: Fertigation 60%; F-100: Fertigation 100%; F-0: Rain-fed.

Free Compounds	2014			2015			Sig.		
	F-0	F-60	F-100	F-0	F-60	F-100	TR	Y	Tr*Y
1-butanol	61.69	103.60	70.42	96.40	103.74	83.14	ns	ns	ns
2 + 3-methyl-1-butanol	**115.35b**	**189.26a**	**124.54b**	112.48	116.66	79.92	ns	ns	ns
3 methyl-3-buten-1-ol	58.34	78.15	45.99	72.01	61.08	63.37	ns	ns	ns
3-methyl-1-pentanol	**30.67b**	**45.43a**	**32.10ab**	38.92	50.62	33.44	ns	ns	ns
1-octen-3-ol	11.69	17.23	14.09	nd	nd	5.63	ns	ns	ns
1-octanol	4.50	9.47	6.72	nd	42.65	2.43	ns	ns	ns
Benzyl alcohol	401.09	530.13	457.48	77.56	77.06	88.88	ns	***	ns
2-phenylethanol	429.53	580.79	444.31	161.70	210.27	165.69	ns	*	ns
Alcohols (%)	*39.16%*	*36.47%*	*41.25%*	*16.77%*	*16.07%*	*12.34%*			
Hexanal	372.58	531.85	321.91	585.12	745.93	683.54	ns	ns	ns
(*E*)-2-hexanol	251.89	310.64	175.27	765.94	1060.51	1201.12	ns	*	ns
1-hexanol	277.67	414.76	309.79	545.67	733.08	805.22	ns	ns	ns
(*Z*)-3-hexenol	38.55	51.11	34.12	56.45	83.38	99.64	ns	ns	ns
(*E*)-2-hexenol	144.44	247.58	148.47	436.03	577.62	561.27	ns	*	ns
2-ethyl-1-hexanol	61.25	76.72	55.85	86.45	99.43	46.52	ns	ns	ns
C_6-compounds (%)	*36.19%*	*34.79%*	*32.61%*	*62.08%*	*67.53%*	*72.68%*			
trans-furan linalool oxide	12.30	47.95	14.77	nd	nd	2.99	ns	ns	ns
cis-furan linalool oxide	11.75	nd	8.70	32.50	nd	18.12	ns	ns	ns
cis-piran linalool oxide	51.19	74.85	45.58	31.67	21.36	35.95	ns	ns	ns
trans-piran linalool oxide	**4.70b**	**7.97a**	**2.99b**	nd	nd	2.02	**	ns	ns
Nerol	9.79	12.65	10.32	9.85	nd	6.63	*	**	ns
Geraniol	39.13	47.25	38.28	27.78	25.92	25.74	ns	ns	ns
Diendiol I	42.64	85.65	39.55	30.66	23.60	21.28	ns	*	ns
(*E*)-8-hydroxylinalool	9.48	11.48	13.33	91.08	nd	31.75	ns	ns	ns
3-oxo-7,8-dihydro-α-ionol	**55.61b**	**107.08a**	**59.24b**	82.26	140.21	54.52	ns	ns	ns
Terpenes + C_{13}	*7.89%*	*8.83%*	***7.67%***	*7.95%*	*4.45%*	*4.32%*			
Diethyl malate	5.33	7.62	5.06	nd	5.08	3.46	ns	ns	ns
Methyl vanillate	39.46	73.97	39.99	91.82	98.17	53.12	ns	ns	ns
Esters (%)	*1.49%*	*1.82%*	*1.48%*	*2.39%*	*2.18%*	*1.23%*			
Benzaldehyde	63.23	71.07	54.90	27.73	32.49	8.01	ns	*	ns
Aldehydes (%)	*2.11%*	*1.59%*	*1.81%*	*2.39%*	*2.18%*	*1.23%*			
Butanoic acid	19.54	33.52	24.20	nd	nd	nd	ns	ns	ns
Hexanoic acid	47.02	86.15	76.59	34.00	16.53	51.16	ns	*	ns
€-2-hexanoic acid	19.33	39.01	35.73	13.01	8.67	25.44	ns	*	ns
Octanoic acid	3.40	5.84	4.57	11.38	4.35	3.48	ns	ns	ns
Geranic acid	**12.20b**	**22.05^{a}**	**15.03ab**	26.22	8.91	18.67	ns	ns	ns
Hexadecanoic acid	92.72	180.87	98.29	62.43	158.23	164.69	ns	ns	ns
Volatile acids (%)	*6.48%*	*8.22%*	*8.38%*	*3.82%*	*4.15%*	*5.71%*			
Guaiacol	19.06	27.41	16.11	19.62	21.20	14.35	ns	ns	ns
Eugenol	10.21	16.30	9.05	23.01	19.35	11.21	ns	ns	ns
4-ethyl phenol	6.05	13.67	5.18	nd	nd	6.01	ns	ns	ns
Vanillin	22.99	46.66	28.12	51.40	71.17	21.94	ns	ns	ns
Volatile phenols (%)	*1.94%*	*2.33%*	*1.93%*	*2.44%*	*2.36%*	*1.16%*			
Butyrolactone	102.10	162.38	94.09	69.51	61.75	54.39	ns	ns	ns
Lactones (%)	*3.41%*	*3.63%*	*3.10%*	*1.81%*	*1.30%*	*2.03%*			
Acetoine	39.90	104.01	53.43	78.09	60.44	55.59	ns	ns	ns
Carbonyl compounds (%)	*1.33%*	*2.33%*	*1.76%*	*2.03%*	*1.28%*	*1.21%*			

Level of significance: *, ** and *** indicates significance at $p < 0.05$, $p < 0.01$ and $p < 0.001$ respectively; ns indicates no significant difference. nd: no detected. The bold values with different letters in the same row are significantly different according to Tukey's test ($p < 0.05$).

treatments.

Fig. 2a shows the PCA applied to free fraction of volatiles where 84.93% of the total variance was explained by the first two principal components. The principal component 1 (PC1) explained 57.48% of the variance and the second principal component (PC2) explained 27.46%. The PC1 was corelated with aldehydes, lactones, volatile acids, alcohols and terpenes + C_{13}-norisoprenoids on the positive side, while PC2 was correlated with C_6 compounds, ethyl esters, phenol volatiles and carbonyl compounds. The fertigation treatment F-60 from 2014 was positioned on positive side of PC1, while the F-60 treatment and control (F-0) from 2015 were sited on positive side of PC2.

Fig. 2b shows the PCA applied to bound fraction of volatiles. The principal component 1 (PC1) explained 60.71% of the variance and the second principal component (PC2) explained 20.70% of the variance,

Table 4
Glicosidically bound composition of Albariño grapes by individual compounds (μg/L) and by groups (%) from fertigation treatments and control (2014–2015). F-60: Fertigation 60%; F-100: Fertigation 100%; F-0: Rain-fed.

Bound compounds	2014			2015			Sig.		
	F-0	F-60	F-100	F-0	F-60	F-100	Tr	Y	Tr*Y
1-butanol	14.42	17.55	24.32	35.36	7.63	17.34	ns	ns	ns
2 + 3-methyl-1-butanol	9.82	13.84	14.73	14.60	3.83	6.23	ns	ns	ns
3 methyl-3-buten-1-ol	8.37	7.00	9.01	9.25	4.52	8.85	ns	ns	ns
3-methyl-1-pentanol	6.48	5.45	4.75	5.40	2.75	5.31	ns	ns	ns
Benzylalcohol	245.06	295.71	330.51	100.75	33.16	52.96	ns	***	ns
2-phenylethanol	132.80	188.19	190.74	121.62	40.88	52.25	ns	***	ns
2-phenoxyethanol	4.14	3.13	2.93	2.26	nd	nd	ns	ns	ns
Alcohols (%)	*19.82%*	*23.40%*	*23.21%*	*11.95%*	*10.17%*	*8.93%*			
1-hexanol	30.10	30.26	26.46	25.38	7.33	11.96	ns	ns	ns
(*E*)-2-hexanol	13.66	12.33	15.28	16.74	4.71	8.84	ns	ns	ns
(*E*)-3-hexenol	**6.37a**	**4.86ab**	**4.35b**	6.25	2.58	5.55	ns	ns	ns
(*Z*)-2-hexenol	10.72	16.57	14.64	17.09	3.83	6.49	ns	ns	ns
(*E*)-2-hexenol	7.49	nd	nd	nd	1.38	6.21	ns	ns	ns
2-ethyl-1-hexanol	14.49	10.29	6.15	8.48	8.46	9.07	ns	ns	ns
C_6-compounds (%)	*3.90%*	*3.28%*	*2.69%*	*3.05%*	*3.10%*	*3.01%*			
trans-furan linalool oxide	10.02	12.14	31.33	8.32	6.49	4.18	ns	ns	ns
cis-furan linalool oxide	40.40	6.10	6.92	15.55	3.38	7.30	ns	ns	ns
Linalool	24.43	12.00	10.29	14.98	9.18	5.48	ns	ns	ns
Hotrienol	7.90	3.58	4.94	4.39	3.35	2.51	ns	ns	ns
trans-piran linalool oxide	17.02	23.03	19.75	18.73	8.67	16.90	ns	ns	ns
cis-piran linalool oxide	6.70	2.45	2.72	2.29	3.98	2.90	ns	ns	ns
β-citronelol	18.78	3.83	5.95	2.73	11.06	7.11	ns	ns	ns
Geraniol	35.79	37.62	39.19	35.95	19.63	30.00	ns	ns	ns
α-ionone	8.10	3.87	3.52	5.10	1.17	4.26	ns	ns	ns
Diendiol-1	56.88	92.34	75.16	81.38	18.51	24.03	ns	ns	ns
Diendiol II	1.42	3.53	5.17	2.91	nd	nd	ns	ns	ns
(*E*)-8-hydroxylinalool	219.31	32.67	39.02	67.17	117.81	19.11	ns	ns	ns
(*Z*)-8-hydroxylinalool	105.36	136.26	132.11	65.90	24.70	29.66	ns	*	ns
3-hydroxy- β -damascone	40.61	59.06	57.96	65.13	20.98	22.47	ns	ns	ns
3-oxo- α -ionol	148.28	197.42	231.15	322.75	63.55	170.74	ns	ns	ns
3-oxo-7,8-dihydro- α -ionol	47.04	67.44	61.09	71.50	31.97	62.42	ns	ns	ns
3-hydroxy-7,8-dehydro- β -ionol	33.05	43.98	45.38	87.68	22.21	nd	ns	ns	ns
Terpenes + C_{13} (%)	*38.65%*	*32.50%*	*31.04%*	*38.10%*	*40.20%*	*25.55%*			
Methyl vanillate	39.58	52.90	55.35	62.85	24.70	29.64	ns	ns	ns
Diethyl succinate	16.27	22.86	28.39	18.65	11.85	13.74	ns	ns	ns
Hexyl acetate	7.94	2.75	2.39	nd	1.14	3.18	*	*	ns
Esters + acetates (%)	*3.00%*	*3.46%*	*3.46%*	*3.37%*	*4.13%*	*2.91%*			
Isobutiric acid	5.29	3.65	3.92	5.10	nd	4.69	ns	ns	ns
Butanoic acid	33.58	39.49	37.45	45.07	6.55	69.89	ns	ns	ns
Hexanoic acid	113.71	155.74	198.81	91.67	33.64	57.24	ns	**	ns
(*E*)-2-hexanoic acid	106.64	152.21	201.40	85.10	41.57	68.41	ns	*	ns
Octanoic acid	5.63	5.72	6.50	5.68	4.85	5.93	ns	ns	ns
Nonanoic acid	5.15	4.67	5.14	5.42	3.48	5.39	ns	ns	ns
Geranic acid	64.14	47.57	46.47	56.72	32.61	46.71	ns	ns	ns
Dodecanoic acid	nd	nd	nd	16.32	7.62	52.15	ns	ns	ns
Hexadecanoic acid	304.32	347.92	381.71	549.61	171.03	389.59	ns	ns	ns
Volatile acids (%)	*30.05%*	*33.37%*	*35.47%*	*35.35%*	*33.04%*	*43.73%*			
Eugenol	13.23	9.52	9.02	9.38	6.54	6.65	ns	ns	ns
4-vinylguaiacol	29.61	31.57	37.11	34.83	36.32	188.77	ns	ns	ns
Vanillin	14.27	24.72	27.05	12.90	15.73	19.78	ns	ns	ns
4-vinylphenol	28.54	16.15	19.64	14.52	19.48	29.20	ns	ns	ns
Volatile phenols (%)	*4.03%*	*3.61%*	*3.73%*	*7.76%*	*8.56%*	*15.27%*			
Butyrolactone	11.59	8.42	9.89	5.72	7.16	9.72	ns	ns	ns
Lactones (%)	*0.55%*	*0.37%*	*0.40%*	*0.24%*	*0.79%*	*0.61%*			

Level of significance: *, ** and *** indicates significance at $p < 0.05$, $p < 0.01$ and $p < 0.001$ respectively; ns indicates no significant difference. nd: no detected. The bold values with different letters in the same row are significantly different according to Tukey's test ($p < 0.05$).

accounted together 81.41% of the variance. The PC1 was corelated with volatile acids, ethyl esters, terpenes, alcohols and C_6-compounds on their positive side, while PC2 was correlated with phenol volatiles on the positive side and lactones on the negative one. The fertigation treatments F-60 and F-100 from 2014 were positioned on positive side of PC1. Control samples (F-0) from 2014 and 2015 were positioned on negative and positive sides of PC2 respectively.

The results showed a different behavior according to vintage, where 2014 accounted higher concentration of positive volatile families. A trend to increase the total positive compounds concentration for F-60 in

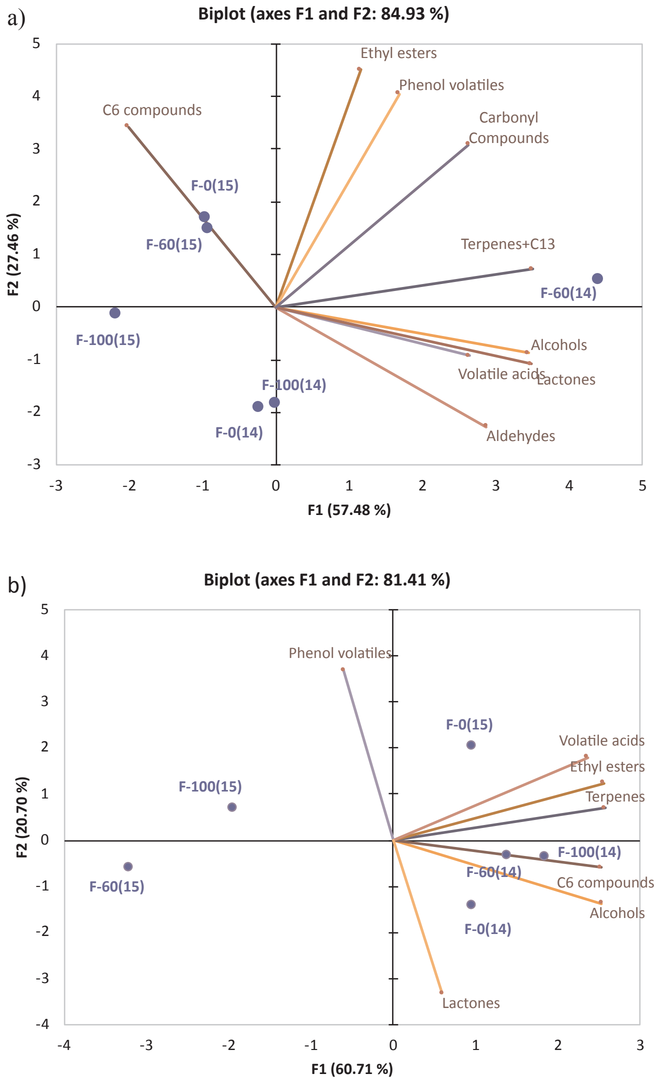

Fig. 2. Principal components analysis (PCA) on volatile families of compounds in free (a) and bound (b) fractions among fertigation treatments and vintages (2014–2015). F-60: Fertigation 60%; F-100: Fertigation 100%; F-0: Rain-fed.

free fraction (2014) and F-100 and F-60 in bound fraction (2014) was observed.

4. Conclusion

Fertigation is a common strategy to supply the water and nutrient requirements of grapevines. This study provides new data about the effect of fertigation treatment application on chemical composition (volatile and non-volatile compounds) of white *cv* Albariño (NW Spain). The results obtained showed that must physicochemical parameters were not affected by fertigation treatment. However, a higher effect of fertigation treatment on free than bound fraction of volatiles was observed when they were compared with a control. Free higher alcohols and terpenoids were the most affected of volatile groups by the irrigation treatments. In general, a trend to increase the volatiles was observed when fertigation treatment was applied, mainly in 2014 vintage, showing a higher vintage effect. The amount and distribution of precipitation in both years, has caused a different effect of fertigation treatments, in relation to the aromatic concentrations present in the musts. Therefore, the management of fertigation treatments should take into account these climatic patterns.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2018.11.105.

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