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Different water and light regimes affect ionome composition in grapevine (*Vitis vinifera* L.)

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Summary

Many inorganic cations play a major role in winemaking processes and wine quality. For this reason, chemistry at the elemental level ("ionomic") of the grape berry is of concern not only to the viticulturist, but also to the oenologist due to their direct impact on juice and must composition, which in turn affect wine quality. The aim of this research was to evaluate the effect of reduced irrigation and incident light (by means of micronized calcite) on the berry skin ionome of the Italian red grape 'Aglianico'. The study was carried out in a five-years-old vineyard (*Vitis vinifera* L. 'Aglianico') located in Southern Italy. Half of the plants (IRR) were drip irrigated, whereas the other half were not irrigated (NIR). Half of IRR and NIR plants were treated with Megagreen® micronized calcite. In all the treatments, plant water status and gas exchange were determined. The mean values of stem water potential (ψ_w) during the experiment were –1.02 and –1.10 MPa in IRR and NIR, respectively. The calcite treatments did not show changes in ψ_w values if compared to the untreated ones. The values of gas exchange were not statistically different among the four treatments. Grape berries were separated into three groups of mass, and the levels of macroelements, microelements and lanthanides were measured. Irrigation and calcite significantly affected macroelements distribution in all the three groups of mass, with Fe, Cu and Zn being significantly higher in the IRR and calcite-treated treatments. The effect of irrigation on the changes in microelement levels was significant for some elements. Calcite-treated vines showed higher mean values of Co, Cd, Hg and Pb. Regarding lanthanides, in calcite-untreated vines, irrigation determined significant decreases in average La, Ce, Nd, whereas in calcite-treated vines, increases in the mean concentrations of Ce, Nd, Sm, Gd, Dy, Er and Yb were found. Generally, lanthanide levels did not change between calcite-treated and untreated vines, and in all the treatments Lu resulted to be the most abundant one. Macroelements, microelements and lanthanide levels generally decreased with decreasing berry weight. The dynamics of the extractability of metals from grape berries to must during fermentation could be used to predict wine quality during the following processes and for wine traceability purposes.

Key words: 'Aglianico', ionome, irradiance, irrigation, metals.

Abbreviations: A_n = net photosynthesis; E = transpiration; ETc = cultural evapotranspiration; ETo = reference evapotranspiration; g_s = stomatal conductance; IRR = irrigated plants; IRR-NT = irrigated plants not treated with calcite; IRR-T = irrigated plants treated with calcite; NIR = non-irrigated plants; NIR-NT = non-irrigated plants not treated with calcite; NIR-T = non-irrigated plants treated with calcite (NIR-T); PPFD = photosynthetic photon flux density; VPD = leaf-to-air vapour pressure deficit; ψ_w = stem water potential.

Introduction

Grape and wine chemistry at the elemental level ("ionomic") includes the content of all mineral nutrients and trace elements. Many inorganic cations play a major role in winemaking processes and wine quality. For instance, in grapes and wines, an excess of macroelements, such as Ca, Fe and/or Cu is responsible for wine turbidity, so playing a major role in winemaking and wine quality (Jackson 2000, Ribéreau-Gayon *et al.* 2006).

At naturally occurring levels, many plant microelements, such as Cr, Co and Se, are important cofactors in human vitamins and enzymes (White 2003). Among micro-elements, heavy metals, naturally present as sulfides in trace, non-toxic concentrations in grapes and wines, become toxic at higher doses and thus their study is important for wine toxicology purposes. The content of stilbenes (e.g. resveratrol), anthocyanins, flavonols and other antioxidant polyphenols in wine vary considerably on the basis of the HMs levels in grapes (Püssa *et al.* 2006). Furthermore, the studies on HMs are of particular importance for grapevine, as the compost often used in vineyards may be a source of toxic levels of Pb and Cd, and municipal solid-waste compost and organic mulches have seen limited use in viticulture due to potential contamination with HMs (Pinamonti 1998). Lanthanides are a homogeneous group of elements having great chemical similarities that occur in general as trivalent cations with exceptions concerning in particular Ce^{+4} and Eu^{+2}. These elements, biologically similar to Ca, affect the stability and functionality of membranes and regulate photosynthetic processes, and 57 % of grapevine berry lanthanides are localized in the skin (Bertoldi *et al.* 2009).

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The metal composition of the grape berry is of concern not only to the viticulturist, but also to the oenologist due to their direct impact of berry nutrition on juice and must composition, which in turn affect wine quality (Rogiers *et al.* 2006). This notwithstanding, grape and wine ionomics is a poorly studied sector. In the last years, studies on metal ionome were carried out in wine (Galgano *et al.* 2008, Volpe *et al.* 2009, Bentlin *et al.* 2011), mainly focusing on wine fingerprinting to detect its provenance. Only recently, Bertoldi *et al.* (2009) and Yang *et al.* (2010) studied lanthanides levels in grapevine berry tissues but without considering the physiological status of the vines and the influence of external factors on their accumulation.

All of the natural inorganic cations in grape, must and wine (*i.e.* excluding those deriving from fertilizers, pesticides and winemaking equipment containing particular alloys) are usually present at non-toxic concentrations for humans (Volpe *et al.* 2009) but their levels can be strongly affected by the agronomic practices adopted in the vineyard and by the environmental parameters experienced by the vines. Low water availability and high light levels are the most important limiting factors for grapevine cultivation in mediterranean areas (Sofo *et al.* 2005). For this reason, the aim of our research is to evaluate the effect of reduced irrigation and the application of micronized calcite (a brownish, non-porous, non-swelling, non-abrasive, chemically inert fine-grained mineral sprayed as a suspension on leaf surface and forming a particles film that reduces light absorption by the berry) on the berry skin ionome of the red grape 'Aglianico', one of the most important cultivar of Southern Italy, whose wine is appreciated worldwide (Manfra *et al.* 2011, Sofo *et al.* 2012). We hypothesize that changes in plant water status and/or subjected to lower incident radiation could determine differences in the metal levels of berry skin, one of the most important mineral sink of grapevine (Rogiers *et al.* 2006), whose mineral compositions strongly affect wine composition and quality (Manfra *et al.* 2011).

Material and Methods

Experimental site and plant material: The experiment was carried out in 2008, from bud break to the harvest, in a five-year-old vineyard ('Aglianico' clone VCR11 grafted on 1103 Paulsen) sited on a clay-loam soil in Montegiordano Marina (42°02' N, 16°35' E; Southern Italy). According to Winkler, this is a climatic region 5, named 'very hot', with a thermic summation of 2603 °C above the threshold of 10 °C between 1 April and 31 October. The experimental plot, of about 0.30 ha, consisted of ten rows of spur-pruned vines to a permanent horizontal unilateral cordon. Each vine, decked at 0.60 m above the ground, was characterized by about 8 spurs of 2 to 3 buds each. The distance between the vines was of 2.5 x 1.0 m, with a final plant density of 4,000 vines·ha^{-1}. Rows were north-south oriented. Half of the vines (IRR) were irrigated from 9 June to 1 August (from early stages of fruit set to véraison) using a water amount equal to 100 % of cultural evapotranspiration (ETc) (24 L per plant per each of ten irrigation turn at approximately 5-d intervals), whereas the other half were not irrigated (NIR). The value of ETc was calculated using ETo x Kc, where ETo is the reference evapotranspiration calculated according to Hargreaves method, and Kc is the cultural coefficient, equal to 0.6 for grapevine during the experimental period, according to Allen *et al.* (1998). The watered plot irrigation started when the stem water potential (ψ_w) was lower than -0.8 MPa and ended around véraison. The seasonal irrigation volume was of 960 m^3 ha^{-1} (240 L·plant^{-1}), each vine was irrigated by two drip emitter per plant discharging 4 L·h^{-1} each.

Half of IRR plants and half of NIR grapevine plants received three foliar applications of Megagreen® micronized calcite (Tribo Technologies, Soultz sous Forêts, France; European Patent N° WO/2000/064586; chemical composition: total carbonate 823.0 g·kg^{-1}; SiO_2 85.2 g·kg^{-1}; MgO 30.2 g·kg^{-1}; Fe 8.78 g·kg^{-1}, and other trace elements). This product is elaborated from a sedimentary limestone rock, which is finned and activated by tribomechanical process that reduces the size of the particles to few micron and increases their exchange surface. The first application was carried out on the June 26, at the beginning of cluster closure [stage 32 of the Eichhorn and Lorenz phenological stages, as modified by Coombe (1980)], the second and the third ones were done thirty (end of véraison) and sixty days later respectively. Megagreen® was applied at 1.00 % (w/v), corresponding to 1.50 kg^{-1}.

Therefore, we had four treatments: irrigated plants treated not treated with calcite (IRR-NT), irrigated plants treated with calcite (IRR-T), non-irrigated plants treated with calcite (NIR-NT), and non-irrigated plants not treated with calcite (NIR-T).

Meteorological variables were monitored by a weather station placed within 50 m of the experimental plot. Measurements of temperature, rainfall, and photosynthetic photon flux density (PPFD) were taken throughout the experimental period. The values of PPFD were recorded at 1-h intervals, and daily integrated values were logged. Leaf-to-air vapour pressure deficit (VPD) was calculated according to Goudrian and Van Laar (1994).

Environmental parameters: The experimental period was characterized by high temperatures and scarcity of rainfall. Maximum temperatures ranged between 15.3 and 38.5 °C, with maximum peaks occurring in the period from the end of July to the beginning of August, in correspondence to grape véraison. Minimum temperatures ranged between 12.3 °C and 29.1 °C. Average annual rainfall was 245 mm, but during the experimental period it was particularly low, with 21.87 mm, with the most relevant rainfall (7.68 mm) on 28 August. Daily values of reference crop evapotranspiration (ETo) fluctuated between 1.06 and 6.82 mm, with the higher values in the first ten days of July and the lower at the end of September. Total daily radiation (PPFD) ranged between 2 and 32 MJ·m^{-2}, showing higher values before 14 September, followed by a sharp decrease after this date. The values of VPD were higher between 26 June and 10 September (maximum of 3.59 kPa on 22 August), whereas they decreased after this period.

Plant water status and gas exchange: The plant water status was determined throughout the experimental period on ten vines per treatment by measurements of stem water potential (ψ_w). Vines located in the central part of the row, where microclimatic conditions and soil physico-chemical characteristics were similar, were chosen. The values of ψ_w were measured around midday on 5 fully expanded and well-lightened leaves selected from each plant on fruiting shoots situated in the median zone of the plant using a pressure chamber (PMS Instrument Co., Corvallis, OR, USA, model 600). For the determination of ψ_w, leaves were covered with aluminium foil and a polyethylene bag at least two hour before each measurement for avoiding transpiration (Choné *et al.* 2001).

For each treatment, the same ten vines used for ψ_w measurements were chosen to measure gas exchange on five fully expanded and well-lightened leaves selected from each plant on fruiting shoots situated in the median zone of the cordon. Gas exchange measurements were carried out on 5 August and 4 September using a portable Li-6400 photosynthesis system (Li-Cor, Lincoln, NE, USA) equipped with a 362-cm^2 wide leaf chamber. Light was provided by an artificial red LED source emitting at 670 nm, and an external bottled 12-g CO_2 source was used to infiltrate the leaf chamber with air at a constant 370 $\mu mol \cdot mol^{-1}$ CO_2.

Metals and metalloids determination: At harvest, on 27 September 2008, three clusters per plant were randomly sampled in the central and well-irradiated area of the canopy from three vines located in the central part of the rows in order to minimize soil differences between the two treatments. All the berries of these clusters were picked and separated into three ranges of mass (x): $x < 0.90$ g, $0.90 \text{ g} \leq x < 1.25$ g, and $x \geq 1.25$ g. The berries were washed three times with ultrapure distilled water, peeled by means of a titanium blade scalpel (Titanium Scalpel #11; Dedham, MA, USA), and the skin rapidly frozen at -80 °C, and then stored.

An aliquot (5 g) of frozen berry skins was digested in a HNO_3:H_2O_2 solution (5:1, v/v) using a high performance microwave digestion unit (MLS-1200 Mega, Milestone Inc., CT, USA). Two milliliters of HNO_3 (0.1 M) were added and then the solution was made up to a 10 mL with ultrapure distilled water. The levels of macroelements, microelements and lanthanides were determined by means of quadrupole inductively coupled plasma mass spectrometry, ICP-QMS (Elan DRC II, Perkin-Elmer SCIEX, CT, USA). Operational parameters were the following: sample uptake rate, 1 $mL \cdot min^{-1}$; sample introduction system, Meinhard nebulizer with cyclonic spray chamber; gas flow rates ($L \cdot min^{-1}$): plasma, 15; auxiliary, 1.0; nebulizer, 0.85; dwell time, 50 msec; interface, Pt cones; extraction lens voltage, optimized for maximum detector response (^{56}Fe). High purity He (99.9999 %) and H_2 (99.9995 %) were used, in order to minimize the potential problems caused by unidentified reactive contaminant species in the cell. The instrument was equipped with an octopole ion guide enclosed in a collision/reaction cell. Moreover, the instrument was operated in an air-conditioned laboratory (20-22 °C) equipped with a filter to remove dust particles. Non-metallic devices were always used to collect and transport the samples. Considering that the instrument used is a simultaneous ICP-QMS, having an array of photo multiplier tubes positioned to look at a fixed set of elements (wavelengths), the reference wavelengths for each metal and metalloid were automatically chosen by the instrument software in order to avoid interferences with the other elements analyzed. As inaccurate results for Hg levels are generally obtained when pneumatic nebulization is used to introduce the sample in the ICP-QMS, we decided to use the method of Jian *et al.* (2000) for Hg determination.

Before use, all glassware and plastic containers were cleaned by washing with 10 % ultra-pure grade HNO_3 for at least 24 h, and then rinsed copiously with ultra-pure water before use. The calibration solutions were prepared from multi-elemental standard stock solutions of 1000 mg L^{-1}, and the calibration curves were obtained by using at least 6 calibration solutions. Reagent blanks containing ultrapure water were additionally analysed in order to control the purity of the reagents and the laboratory equipment.

The metals and metalloids analyzed were divided in macroelements (> 100 $\mu g \cdot kg^{-1}$ dry berry skin), microelements (< 100 $\mu g \cdot kg^{-1}$ dry berry skin) and lanthanides.

Statistical analysis: The data on ψ_w, gas exchange were represented as the means of ten separate measurements on ten different vines per treatment, with five replicates per plant ($n = 50$). The data on metal levels were represented as the means of three separate measurements on three different vines per treatment, with ten replicates ($n = 30$).

Statistical analysis was performed by analysis of variance (ANOVA) with SAS software (SAS Institute, Cary, NC, USA). Significant differences were determined at $P \leq 0.001$, according to Fisher's LSD test.

Results

Plant water status and gas exchange: At the beginning of the experiment, the values of stem water potential (ψ_w) measured in IRR and NIR were -0.56 and -0.67 MPa, respectively, then ψ_w decreased linearly till 8 July and remained stable till the end of the experimental period. The mean ψ_w values were -1.02 and -1.10 MPa in IRR and NIR, respectively, statistically different between the two treatments ($P \leq 0.001$). In general, the calcite treatments were ineffective with respect to ψ_w values, with the exception of three dates when calcite-treated vines have shown a significant higher value of xylem water potential if compared to the untreated ones.

Net photosynthesis (A_n) in IRR and NIR was 2.71 and 2.32 $\mu mol\ CO_2\ m^{-2} \cdot s^{-1}$ on 5 August, respectively, and 5.80 and 5.69 $\mu mol\ CO_2\ m^{-2} \cdot s^{-1}$ on 4 September, and no significant differences were found between the two treatments ($P \leq 0.001$). Transpiration (E) in IRR and NIR was 1.89 and 2.11 $mmol\ H_2O\ m^{-2} \cdot s^{-1}$, respectively, on 5 August, and 3.60 and 3.86 $mmol\ H_2O\ m^{-2} \cdot s^{-1}$, respectively, on 4 September, without any statistical differences between the two treatments ($P \leq 0.001$). The values of stomatal conduct-

ance (g_s) measured on 5 August was 0.03 mol H_2O $m^{-2}·s^{-1}$ in both IRR and NIR, and 0.08 and 0.09 mol H_2O $m^{-2}·s^{-1}$ on 4 September in IRR and NIR, respectively, and no significant differences between the two treatments were revealed ($P \leq 0.001$). In both IRR and NIR, the treatment with calcite did not significantly affect plant gas exchange.

Macroelements: Generally, irrigation and calcite significantly affected macroelement distribution in all of the three groups of mass (Tab. 1). The average levels of Fe, Cu and Zn were significantly higher in the IRR treatments, and calcite application determined higher levels of these elements. The mean levels of Ca, the most abundant macroelement (approximately 3 mg·kg^{-1} dry berry skin) were not statistically different between the two irrigation treatments nor between calcite-treated and untreated vines. In contrast, Al average content resulted to be lower in the IRR treatments, showing significant differences only in calcite-untreated vines. Macroelement levels significantly decreased with decreasing berry weight (Tab. 1).

Microelements: The effect of irrigation on microelement levels was significant for some elements (Tab. 2). In calcite-untreated vines, irrigation caused significant increases in the mean content of Cr, Ni, Ga, As, Cd, Cs, Pt, Hg, Tl and Pb, and decreases in Ti, V, Se and Sn. In calcite-treated vines, irrigation caused significant increases in the average levels of Ni, Zr, Mo, Cd, In, Te, Cs, Hf, W, Re, Os, Ir, Pt, Hg and Pb, and decreases in Se and Sr content. Regarding the micronutrients essential for humans, in both calcite-treated and untreated vines, the levels of Cr and Co were not affected by irrigation, whereas significant increases in average Se content were observed in NIR vines (Tab. 2). Furthermore, calcite-treated vines showed higher mean values of Co (between 7.26 and 9.20 µg·k^{-1} dry berry skin) if compared to the untreated ones. The average levels of Cd, Hg and Pb were significantly higher in calcite-treated vines and they increased with irrigation (Tab. 2). Microelement levels generally decreased or remained stable with decreasing berry weight, with some exceptions, such as for Cd, Hg, and As, where an opposite trend was observed (Tab. 2).

Lanthanides: In calcite-untreated vines, irrigation determined significant decreases in average La, Ce, Nd, whereas in calcite-treated vines this effects appeared to be reversed, with significant increases in the mean concentrations of Ce, Nd, Sm, Gd, Dy, Er and Yb (Tab. 3). Generally, there were no significant differences in the lanthanide levels between calcite-treated and untreated vines, and in all the treatments Lu resulted to be the most abundant one (approximately 1 µg·kg^{-1} dry berry skin) (Tab. 3). The levels of RREs significantly decreased with decreasing berry weight, with some exceptions in which they remained stable (Tab. 3).

Discussion

The study of grape ionomics is important for obtaining good quality grapes and wines. For instance, *Saccharomyces* species, can grow on a minimal range of organic and inorganic nutrients, and only optimal and balanced amounts of macroelements, microelements and lanthanides, provide the necessary nutrients for their growth and reproduction (Ugliano and Henschke 2009). Generally, our results showed that metal levels significantly decreased with increasing berry weight (Tabs 1-3). In grapevine, metals are mainly co-transported with water from the soils, via the xylem, to the fruits, and most of the berry volume gain before *véraison* is due to water import from the xylem, whereas most of the post-*véraison* gain is due to water import from the phloem (Rogiers *et al.* 2006, Conde *et al.* 2007). This perhaps depends more on source and/or sink behavior than on physical loss in xylem conductance. On this basis, the

Table 1

Levels of macroelements in berry skins of irrigated (IRR) and non-irrigated (NIR) grapes, treated (T) and not treated (NT) with calcite. Mean values (n = 30; ± st. dev.) followed by different letters are significantly different (uppercase between berry mass ranges within the same treatment, and lowercase between the average values of the different treatments) at $P \leq 0.001$, according to Fisher's LSD test

Treatment	Group of berry mass (x) (g)	Al	Ca	Fe	Cu	Zn
		(µg·kg^{-1} dry berry skin)				
IRR-NT	x<0.90	105.94 ± 30.80 A	3926.85 ± 278.32 A	426.41 ± 63.96 A	324.74 ± 70.47 A	578.97 ± 78.32 A
	0.90≤ x<1.25	71.87 ± 6.81 B	3091.84 ± 403.44 B	150.76 ± 40.90 B	251.81 ± 14.07 B	453.84 ± 43.44 A
	x≥1.25	65.11 ± 5.77 B	2970.95 ± 313.89 B	145.48 ± 22.16 B	138.04 ± 21.11 C	380.58 ± 33.89 B
	Average	*80.97 ± 21.89 c*	*3329.88 ± 520.51 a*	*240.88 ± 38.03 b*	*238.20 ± 94.09 b*	*471.13 ± 100.32 b*
NIR-NT	x<0.90	239.11 ± 21.35 A	3946.33 ± 323.49 A	81.14 ± 23.96 A	152.06 ± 45.46 A	335.49 ± 38.40 A
	0.90≤x< 1.25	234.00 ± 47.57 A	2513.50 ± 223.42 B	80.56 ± 20.90 A	126.35 ± 44.94 A	272.94 ± 13.42 A
	x≥1.25	147.24 ± 33.54 B	2587.70 ± 488.40 B	30.62 ± 12.16 B	59.12 ± 12.88 B	209.43 ± 13.49 B
	Average	*206.78 ± 51.63 a*	*3015.84 ± 806.68 a*	*64.11 ± 29.00 d*	*112.51 ± 47.99 d*	*238.20 ± 94.09 d*
IRR-T	x<0.90	128.60 ± 32.52 A	2750.23 ± 628.77 A	499.12 ± 74.70 A	794.39 ± 68.70 A	1106.48 ± 248.01 A
	0.90≤x<1.25	118.00 ± 5.35 A	2489.02 ± 455.95 B	356.91 ± 45.58 A	557.51 ± 82.79 B	779.09 ± 213.16 B
	x≥1.25	97.12 ± 23.21 B	2490.58 ± 654.13 B	273.57 ± 87.53 B	468.49 ± 91.47 B	768.19 ± 115.94 B
	Average	*114.57 ± 16.02 b*	*2909.94 ± 519.53 a*	*376.53 ± 114.05 a*	*606.80 ± 168.45 a*	*884.59 ± 192.24 a*
NIR-T	x<0.90	148.44 ± 18.72 A	3442.24 ± 1710.84 A	236.63 ± 53.47 A	274.97 ± 81.43 A	787.30 ± 177.72 A
	0.90≤x<1.25	117.72 ± 31.62 B	3094.49 ± 1232.41 A	133.82 ± 24.90 B	212.25 ± 50.16 B	689.21 ± 202.63 A
	x≥1.25	105.10 ± 13.39 B	2808.35 ± 538.31 B	118.35 ± 32.11 B	194.10 ± 39.78 B	595.68 ± 117.01 B
	Average	*123.75 ± 22.29 b*	*3115.03 ± 317.44 a*	*162.93 ± 64.29 c*	*227.10 ± 42.43 c*	*690.73 ± 95.82 c*

Table 2

Levels of microelements in berry skins of irrigated (IRR) and non-irrigated (NIR) grapes, treated (T) and not treated (NT) with calcite. Mean values (n = 30; ± st. dev.) followed by different letters are significantly different (uppercase between berry mass group within the same treatment, and lowercase between the average values of the different treatments) at $P \leq 0.001$, according to Fisher's LSD test

Treatment	Group of berry mass (x) (g)	Ti	V	Cr	Mn	Co	Ni
		(µg·kg^{-1} dry berry skin)					
IRR-NT	x<0.90	15.52 ± 2.46 A	19.06 ± 1.14 A	19.89 ± 2.53 A	9.38 ± 2.17 A	5.75 ± 1.17 A	19.97 ± 5.37 A
	0.90≤ x<1.25	16.45 ± 4.73 A	18.36 ± 3.98 A	15.90 ± 4.29 B	7.83 ± 2.83 A	6.19 ± 1.15 A	12.84 ± 3.77 B
	x≥1.25	15.92 ± 3.79 A	15.38 ± 4.52 B	15.76 ± 3.97 B	4.99 ± 0.83 B	3.44 ± 0.52 B	11.67 ± 4.49 B
	Average	*15.96 ± 0.47 b*	*17.60 ± 1.95 b*	*17.18 ± 2.35 a*	*7.40 ± 2.23 a*	*5.13 ± 1.48 b*	*14.83 ± 4.49 b*
NIR-NT	x<0.90	54.17 ± 4.88 A	43.11 ± 4.13 A	14.93 ± 2.49 A	9.25 ± 1.56 A	11.00 ± 2.09 A	12.16 ± 2.55 A
	0.90≤x< 1.25	47.33 ± 3.57 A	35.85 ± 2.38 B	13.55 ± 2.21 A	10.22 ± 2.65 A	5.37 ± 1.40 B	10.90 ± 1.67 A
	x≥1.25	36.60 ± 4.48 B	36.78 ± 4.33 B	10.53 ± 1.77 B	5.56 ± 1.88 B	3.01 ± 0.29 B	5.42 ± 1.72 B
	Average	*46.03 ± 8.86 a*	*38.58 ± 3.95 a*	*13.00 ± 2.25 b*	*8.34 ± 2.46 a*	*4.19 ± 1.67 b*	*9.49 ± 3.58 c*
IRR-T	x<0.90	16.79 ± 4.35 A	35.93 ± 1.27 A	17.91 ± 1.02 A	24.58 ± 3.00 A	13.08 ± 0.73 A	46.26 ± 9.56 A
	0.90≤x<1.25	16.80 ± 0.71 A	34.28 ± 2.77 A	13.88 ± 3.28 B	12.45 ± 2.81 B	6.98 ± 1.34 B	41.23 ± 6.73 B
	x≥1.25	15.60 ± 2.67 A	33.80 ± 2.00 A	15.12 ± 1.29 B	7.54 ± 1.25 C	7.55 ± 1.92 B	26.31 ± 7.96 B
	Average	*16.40 ± 0.69 b*	*34.67 ± 1.12 a*	*15.64 ± 2.06 a*	*9.20 ± 3.37 a*	*9.20 ± 3.37 a*	*37.93 ± 10.38 a*
NIR-T	x<0.90	39.88 ± 5.75 A	35.03 ± 5.18 A	19.85 ± 3.98 A	8.12 ± 2.32 A	9.52 ± 1.19 A	17.74 ± 5.11 A
	0.90≤x<1.25	37.72 ± 9.67 A	32.80 ± 6.15 A	17.09 ± 1.28 A	9.12 ± 2.52 A	7.41 ± 1.22 A	10.93 ± 2.81 B
	x≥1.25	22.92 ± 6.15 B	19.93 ± 4.28 B	13.81 ± 2.92 B	2.82 ± 0.39 B	4.86 ± 0.78 B	7.17 ± 2.09 C
	Average	*33.51 ± 9.23 a*	*29.25 ± 8.15 a*	*16.92 ± 3.02 a*	*6.69 ± 3.39 a*	*7.26 ± 2.33 a*	*11.94 ± 5.36 b*
Treatment	Group of berry mass (x) (g)	Zr	Nb	Mo	Ru	Pd	Ag
		(µg·kg^{-1} dry berry skin)					
IRR-NT	x<0.90	0.66 ± 0.05 A	0.17 ± 0.03 A	9.57 ± 2.49 A	0.12 ± 0.02 A	2.21 ± 0.16 A	2.71 ± 0.38 A
	0.90≤ x<1.25	0.47 ± 0.05 B	0.09 ± 0.02 B	8.20 ± 2.94 A	0.13 ± 0.02 A	2.24 ± 0.14 A	2.79 ± 0.75 A
	x≥1.25	0.38 ± 0.07 C	0.10 ± 0.03 B	5.26 ± 1.81 B	0.14 ± 0.03 A	2.20 ± 0.12 A	1.32 ± 0.18 B
	Average	*0.50 ± 0.14 b*	*0.12 ± 0.04 a*	*7.68 ± 2.20 b*	*0.13 ± 0.01 a*	*2.22 ± 0.02 a*	*2.27 ± 0.83 a*
NIR-NT	x<0.90	0.40 ± 0.02 A	0.18 ± 0.04 A	5.69 ± 1.06 A	0.11 ± 0.02 A	2.14 ± 0.19 A	4.84 ± 1.72 A
	0.90≤x< 1.25	0.30 ± 0.03 B	0.06 ± 0.01 B	6.41 ± 1.69 A	0.12 ± 0.03 A	2.28 ± 0.25 A	2.38 ± 0.93 B
	x≥1.25	0.31 ± 0.08 B	0.06 ± 0.02 B	4.00 ± 0.76 B	0.16 ± 0.02 A	2.23 ± 0.29 A	2.80 ± 1.16 B
	Average	*0.34 ± 0.06 c*	*0.10 ± 0.07 a*	*5.37 ± 1.24 b*	*0.13 ± 0.03 a*	*2.21 ± 0.07 a*	*3.34 ± 1.32 a*
IRR-T	x<0.90	1.53 ± 0.21 A	0.30 ± 0.05 A	11.89 ± 1.61 A	0.34 ± 0.08 A	3.04 ± 1.11 A	2.67 ± 0.58 A
	0.90≤x<1.25	1.14 ± 0.45 A	0.11 ± 0.02 B	11.48 ± 2.99 A	0.15 ± 0.01 B	2.32 ± 0.14 A	1.99 ± 0.33 B
	x≥1.25	0.37 ± 0.04 B	0.11 ± 0.03 B	6.83 ± 1.45 B	0.12 ± 0.04 B	2.41 ± 0.18 A	1.42 ± 0.32 B
	Average	*1.01 ± 0.59 a*	*0.17 ± 0.11 a*	*10.07 ± 2.81 a*	*0.20 ± 0.12 a*	*2.59 ± 0.39 a*	*2.03 ± 0.63 a*
NIR-T	x<0.90	0.35 ± 0.08 A	0.20 ± 0.03 A	6.01 ± 1.49 A	0.18 ± 0.03 A	2.18 ± 0.13 A	1.69 ± 0.46 A
	0.90≤x<1.25	0.31 ± 0.05 A	0.06 ± 0.02 B	7.79 ± 0.44 A	0.12 ± 0.04 B	2.24 ± 0.08 A	1.22 ± 0.11 A
	x≥1.25	0.34 ± 0.02 A	0.07 ± 0.01 B	4.99 ± 0.64 B	0.12 ± 0.04 B	2.25 ± 0.22 A	1.39 ± 0.35 A
	Average	*0.33 ± 0.02 c*	*0.11 ± 0.08 a*	*6.26 ± 1.42 b*	*0.14 ± 0.03 a*	*2.22 ± 0.04 a*	*1.43 ± 0.24 a*
Treatment	Group of berry mass (x) (g)	Cs	Ba	Hf	W	Re	Os
		(µg·kg^{-1} dry berry skin)					
IRR-NT	x<0.90	0.20 ± 0.04 A	8.69 ± 1.62 A	0.02 ± 0.01 A	0.44 ± 0.11 A	0.01 ± 0.00 A	0.22 ± 0.04 A
	0.90≤ x<1.25	0.20 ± 0.05 A	6.73 ± 1.60 A	0.02 ± 0.00 A	0.27 ± 0.05 B	0.01 ± 0.00 A	0.13 ± 0.02 B
	x≥1.25	0.19 ± 0.02 A	3.26 ± 1.17 B	0.02 ± 0.00 A	0.33 ± 0.10 B	0.02 ± 0.00 A	0.10 ± 0.03 B
	Average	*0.20 ± 0.01 a*	*6.23 ± 2.75 a*	*0.02 ± 0.00 b*	*0.35 ± 0.09 b*	*0.01 ± 0.01 b*	*0.15 ± 0.06 b*
NIR-NT	x<0.90	0.16 ± 0.03 A	8.87 ± 1.97 A	0.01 ± 0.01 A	0.26 ± 0.06 B	0.01 ± 0.00 A	0.13 ± 0.04 A
	0.90≤x< 1.25	0.14 ± 0.02 A	4.08 ± 0.93 B	0.01 ± 0.01 A	0.38 ± 0.07 A	0.01 ± 0.00 A	0.09 ± 0.02 B
	x≥1.25	0.11 ± 0.02 B	3.91 ± 0.40 B	0.01 ± 0.00 A	0.22 ± 0.02 B	0.01 ± 0.00 A	0.06 ± 0.03 B
	Average	*0.14 ± 0.03 b*	*5.62 ± 2.82 a*	*0.01 ± 0.00 b*	*0.29 ± 0.08 b*	*0.01 ± 0.00 b*	*0.09 ± 0.04 b*
IRR-T	x<0.90	0.42 ± 0.11 A	6.49 ± 1.70 A	0.12 ± 0.07 A	1.44 ± 0.47 A	0.05 ± 0.02 A	0.51 ± 0.10 A
	0.90≤x<1.25	0.19 ± 0.04 B	7.52 ± 2.17 A	0.03 ± 0.01 B	1.43 ± 0.20 A	0.03 ± 0.01 A	0.44 ± 0.08 A
	x≥1.25	0.15 ± 0.04 B	4.61 ± 0.31 B	0.03 ± 0.01 B	1.30 ± 0.28 B	0.03 ± 0.01 A	0.25 ± 0.03 B
	Average	*0.25 ± 0.15 a*	*6.21 ± 1.48 a*	*0.06 ± 0.05 a*	*1.39 ± 0.08 a*	*0.04 ± 0.01 a*	*0.40 ± 0.13 a*
NIR-T	x<0.90	0.16 ± 0.03 A	6.47 ± 1.37 A	0.02 ± 0.01 A	0.27 ± 0.04 B	0.01 ± 0.00 A	0.17 ± 0.02 A
	0.90≤x<1.25	0.14 ± 0.01 A	4.39 ± 1.39 B	0.01 ± 0.00 B	0.30 ± 0.03 B	0.01 ± 0.00 A	0.20 ± 0.04 A
	x≥1.25	0.16 ± 0.00 A	4.01 ± 0.82 B	0.01 ± 0.00 B	0.50 ± 0.18 A	0.01 ± 0.00 A	0.11 ± 0.04 B
	Average	*0.15 ± 0.01 b*	*4.96 ± 1.32 a*	*0.01 ± 0.01 b*	*0.36 ± 0.13 b*	*0.01 ± 0.00 b*	*0.16 ± 0.05 b*

Tab. 2, continued

Treatment	Group of berry mass (x) (g)	Ga	As	Se	Rb	Sr
		(µg·kg^{-1} dry berry skin)				
IRR-NT	x<0.90	1.51 ± 0.27 A	14.24 ± 3.87 A	6.64 ± 1.08 A	37.27 ± 3.11 A	54.93 ± 5.12 A
	0.90≤ x<1.25	1.44 ± 0.36 A	12.88 ± 2.08 A	5.77 ± 1.02 A	37.62 ± 6.45 A	58.24 ± 14.84 A
	x≥1.25	1.50 ± 0.11 A	10.78 ± 1.90 A	5.04 ± 0.67 A	35.32 ± 5.78 A	46.79 ± 13.96 A
	Average	*1.48 ± 0.04 a*	*12.63 ± 1.74 a*	*5.82 ± 0.80 b*	*36.74 ± 1.24 a*	*53.32 ± 5.90 a*
NIR-NT	x<0.90	0.64 ± 0.08 A	4.86 ± 0.40 B	24.26 ± 3.48 A	37.39 ± 4.13 A	57.89 ± 15.71 A
	0.90≤x< 1.25	0.60 ± 0.07 A	7.34 ± 1.94 A	23.26 ± 5.45 A	33.38 ± 8.87 A	54.08 ± 3.02 A
	x≥1.25	0.23 ± 0.04 B	6.49 ± 1.19 A	21.91 ± 3.91 B	30.72 ± 4.54 A	45.50 ± 9.58 A
	Average	*0.49 ± 0.23 b*	*6.23 ± 1.26 b*	*23.14 ± 1.18 a*	*33.83 ± 3.36 a*	*52.49 ± 6.35 a*
IRR-T	x<0.90	2.00 ± 0.26 A	7.85 ± 0.92 A	5.80 ± 0.29 A	34.86 ± 8.34 A	41.97 ± 4.58 A
	0.90≤x<1.25	1.52 ± 0.07 B	4.09 ± 1.29 A	6.19 ± 0.52 A	33.88 ± 4.95 A	40.16 ± 6.60 A
	x≥1.25	1.32 ± 0.20 B	4.47 ± 0.14 A	5.85 ± 0.50 A	26.90 ± 6.86 B	35.88 ± 14.32 A
	Average	*1.61 ± 0.35 a*	*5.47 ± 2.07 b*	*5.95 ± 0.21 b*	*31.88 ± 4.34 a*	*39.23 ± 3.13 b*
NIR-T	x<0.90	1.30 ± 0.26 A	3.02 ± 0.21 B	25.80 ± 3.31 A	37.17 ± 4.03 A	61.86 ± 13.32 A
	0.90≤x<1.25	1.30 ± 0.12 A	4.46 ± 1.81 A	26.19 ± 1.90 A	34.54 ± 9.22 A	61.57 ± 13,46 A
	x≥1.25	1.40 ± 0.08 A	4.26 ± 0.19 A	25.85 ± 3.28 A	31.73 ± 1.67 A	39.80 ± 4.73 B
	Average	*1.33 ± 0.06 a*	*3.91 ± 0.78 b*	*25.95 ± 0.21 a*	*34.48 ± 2.72 a*	*54.41 ± 12.66 a*
Treatment	Group of berry mass (x) (g)	Cd	In	Sn	Sb	Te
		(µg·kg^{-1} dry berry skin)				
IRR-NT	x<0.90	0.15 ± 0.04 B	1.02 ± 0.07 A	12.85 ± 0.69 A	8.54 ± 1.68 A	0.13 ± 0.04 A
	0.90≤ x<1.25	0.20 ± 0.06 A	0.52 ± 0.12 B	12.62 ± 1.65 A	5.69 ± 1.97 B	0.13 ± 0.06 A
	x≥1.25	0.27 ± 0.02 A	0.69 ± 0.20 B	12.68 ± 1.06 A	1.73 ± 0.29 C	0.10 ± 0.03 A
	Average	*0.21 ± 0.06 b*	*0.74 ± 0.25 a*	*12.72 ± 0.12 b*	*5.32 ± 3.42 a*	*0.12 ± 0.02 b*
NIR-NT	x<0.90	0.08 ± 0.02 B	0.83 ± 0.04 A	11.13 ± 3.89 A	6.28 ± 0.40 A	0.10 ± 0.02 A
	0.90≤x< 1.25	0.06 ± 0.00 B	0.50 ± 0.12 B	13.01 ± 4.02 A	8.25 ± 0.53 A	0.11 ± 0.03 A
	x≥1.25	0.14 ± 0.01 A	0.47 ± 0.06 B	13.63 ± 4.79 A	5.43 ± 0.64 B	0.14 ± 0.02 B
	Average	*0.09 ± 0.04 c*	*0.60 ± 0.20 a*	*18.59 ± 1.30 a*	*6.65 ± 1.45 a*	*0.12 ± 0.02 b*
IRR-T	x<0.90	0.21 ± 0.07 B	1.17 ± 0.29 A	15.57 ± 2.00 A	2.29 ± 0.53 A	0.39 ± 0.03 A
	0.90≤x<1.25	0.37 ± 0.09 A	0.79 ± 0.21 B	12.43 ± 0.93 B	1.25 ± 0.40 B	0.26 ± 0.02 B
	x≥1.25	0.40 ± 0.10 A	0.29 ± 0.13 B	12.78 ± 1.02 B	1.77 ± 0.39 B	0.17 ± 0.01 B
	Average	*0.33 ± 0.10 a*	*0.75 ± 0.44 a*	*13.59 ± 1.72 b*	*1.77 ± 0.52 b*	*0.27 ± 0.11 a*
NIR-T	x<0.90	0.14 ± 0.03 B	0.77 ± 0.10 A	13.03 ± 1.11 A	2.43 ± 0.20 A	0.10 ± 0.01 A
	0.90≤x<1.25	0.21 ± 0.05 A	0.56 ± 0.08 B	12.45 ± 0.52 A	1.99 ± 0.17 B	0.08 ± 0.03 A
	x≥1.25	0.29 ± 0.07 A	0.26 ± 0.07 C	13.23 ± 1.09 A	3.00 ± 0.88 A	0.10 ± 0.01 A
	Average	*0.21 ± 0.08 b*	*0.53 ± 0.26 b*	*12.90 ± 0.41 b*	*2.47 ± 0.51 b*	*0.09 ± 0.01 b*
Treatment	Group of berry mass (x) (g)	Ir	Pt	Hg	Tl	Pb
		(µg·kg^{-1} dry berry skin)				
IRR-NT	x<0.90	0.03 ± 0.01 A	0.11 ± 0.02 A	9.21 ± 0.93 B	2.91 ± 0.22 A	32.96 ± 5.41 A
	0.90≤ x<1.25	0.02 ± 0.01 A	0.11 ± 0.03 A	11.20 ± 0.96 A	2.81 ± 0.23 A	17.37 ± 1.62 B
	x≥1.25	0.02 ± 0.00 A	0.09 ± 0.04 A	10.98 ± 3.02 A	2.95 ± 0.19 A	12.61 ± 2.02 B
	Average	*0.02 ± 0.01 b*	*0.10 ± 0.01 b*	*10.46 ± 1.09 b*	*2.89 ± 0.07 a*	*20.98 ± 10.64 a*
NIR-NT	x<0.90	0.01 ± 0.00 A	0.03 ± 0.02 A	6.21 ± 1.82 B	1.30 ± 0.16 A	25.61 ± 7.76 A
	0.90≤x< 1.25	0.01 ± 0.01 A	0.04 ± 0.02 A	8.23 ± 2.01 A	1.80 ± 0.55 A	9.59 ± 3.69 B
	x≥1.25	0.01 ± 0.01 A	0.06 ± 0.03 A	8.55 ± 0.14 A	1.75 ± 0.40 A	6.95 ± 2.08 B
	Average	*0.01 ± 0.00 b*	*0.04 ± 0.02 c*	*7.66 ± 1.27 c*	*1.62 ± 0.28 b*	*14.05 ± 10.10 b*
IRR-T	x<0.90	0.10 ± 0.02 A	0.34 ± 0.08 A	13.41 ± 5.24 C	3.88 ± 1.13 A	40.21 ± 3.71 A
	0.90≤x<1.25	0.07 ± 0.02 A	0.31 ± 0.10 A	23.21 ± 2.01 B	2.61 ± 0.36 B	16.72 ± 1.45 B
	x≥1.25	0.05 ± 0.01 B	0.22 ± 0.05 B	25.96 ± 1.09 A	2.70 ± 0.18 B	15.62 ± 1.51 B
	Average	*0.07 ± 0.03 a*	*0.29 ± 0.06 a*	*20.87 ± 6.60 a*	*3.12 ± 0.71 a*	*25.12 ± 13.89 a*
NIR-T	x<0.90	0.02 ± 0.01 A	0.14 ± 0.04 A	13.22 ± 2.63 B	2.82 ± 0.17 A	25.00 ± 2.07 A
	0.90≤x<1.25	0.02 ± 0.01 A	0.12 ± 0.03 A	14.49 ± 1.43 B	2.72 ± 0.28 A	16.71 ± 0.51 B
	x≥1.25	0.02 ± 0.00 A	0.13 ± 0.01 A	16.74 ± 1.82 A	2.80 ± 0.19 A	15.46 ± 3.42 B
	Average	*0.02 ± 0.00 b*	*0.13 ± 0.01 b*	*14.82 ± 1.78 b*	*2.78 ± 0.05 a*	*19.06 ± 5.18 b*

dilution effects accompanied by no further accumulation after the first phase of berry growth could be the cause of the observed general trend with lower metal levels in the heaviest berries (Tabs 1-3). In NIR treatments, Fe, Cu and Zn levels in berry skins were significantly lower than those found in IRR vines (Tab. 1), confirming that lower irrigation can increase grape (and in turn wine) quality. Indeed, at higher than normal levels, minerals such as Fe and Cu

Table 3

Levels of lanthanides in berry skins of irrigated (IRR) and non-irrigated (NIR) grapes, treated (T) and not treated (NT) with calcite. Mean values (n = 30; ± st. dev.) followed by different letters are significantly different (uppercase between berry mass groups within the same treatment, and lowercase between the average values of the different treatments) at $P \leq 0.001$, according to Fisher's LSD test

Treatment	Group of berry mass (x) (g)	La	Ce	Pr	Nd	Sm	Eu
		(μg·kg^{-1} dry berry skin)					
IRR-NT	x<0.90	0.19 ± 0.05 A	0.33 ± 0.08 A	0.03 ± 0.01 A	0.12 ± 0.03 A	0.04 ± 0.02 A	0.01 ± 0.00 A
	0.90≤ x<1.25	0.18 ± 0.05 A	0.28 ± 0.05 B	0.03 ± 0.01 A	0.10 ± 0.04 B	0.03 ± 0.01 A	0.01 ± 0.00 A
	x≥1.25	0.16 ± 0.08 B	0.26 ± 0.06 B	0.03 ± 0.00 A	0.07 ± 0.02 B	0.02 ± 0.01 B	0.01 ± 0.00 A
	Average	*0.18 ± 0.02 c*	*0.29 ± 0.04 c*	*0.03 ± 0.00 a*	*0.10 ± 0.03 b*	*0.03 ± 0.01 b*	*0.01 ± 0.00 a*
NIR-NT	x<0.90	0.65 ± 0.15 A	1.06 ± 0.14 A	0.10 ± 0.02 A	0.27 ± 0.04 A	0.03 ± 0.01 A	0.01 ± 0.00 A
	0.90≤x< 1.25	0.39 ± 0.06 B	0.52 ± 0.07 B	0.02 ± 0.00 B	0.12 ± 0.04 B	0.02 ± 0.00 B	0.01 ± 0.00 A
	x≥1.25	0.14 ± 0.03 C	0.25 ± 0.05 C	0.04 ± 0.01 B	0.07 ± 0.02 C	0.02 ± 0.01 B	0.01 ± 0.00 A
	Average	*0.39 ± 0.26 a*	*0.61 ± 0.41 a*	*0.05 ± 0.04 a*	*0.15 ± 0.10 a*	*0.02 ± 0.01 b*	*0.01 ± 0.00 a*
IRR-T	x<0.90	0.36 ± 0.09 A	0.82 ± 0.09 A	0.07 ± 0.02 A	0.25 ± 0.05 A	0.09 ± 0.02 A	0.03 ± 0.01 A
	0.90≤x<1.25	0.17 ± 0.04 B	0.25 ± 0.04 B	0.03 ± 0.01 B	0.14 ± 0.03 B	0.04 ± 0.01 B	0.01 ± 0.00 A
	x≥1.25	0.14 ± 0.04 B	0.24 ± 0.08 B	0.02 ± 0.01 B	0.12 ± 0.03 B	0.05 ± 0.02 B	0.01 ± 0.00 A
	Average	*0.22 ± 0.12 b*	*0.44 ± 0.33 b*	*0.04 ± 0.03 a*	*0.17 ± 0.07 a*	*0.06 ± 0.03 a*	*0.02 ± 0.01 a*
NIR-T	x<0.90	0.39 ± 0.11 A	0.51 ± 0.07 A	0.05 ± 0.02 A	0.11 ± 0.03 A	0.02 ± 0.01 A	0.01 ± 0.00 A
	0.90≤x<1.25	0.18 ± 0.05 B	0.26 ± 0.06 B	0.02 ± 0.01 B	0.07 ± 0.02 B	0.02 ± 0.00 A	0.01 ± 0.00 A
	x≥1.25	0.21 ± 0.06 B	0.28 ± 0.05 B	0.02 ± 0.01 B	0.08 ± 0.03 B	0.03 ± 0.00 A	0.01 ± 0.00 A
	Average	*0.26 ± 0.11 b*	*0.35 ± 0.14 c*	*0.03 ± 0.02 a*	*0.09 ± 0.02 b*	*0.02 ± 0.01 b*	*0.01 ± 0.00 a*
Treatment	Group of berry mass (x) (g)	Gd	Dy	Er	Tm	Yb	Lu
		(μg·kg^{-1} dry berry skin)					
IRR-NT	x<0.90	0.03 ± 0.00 A	0.02 ± 0.01 A	0.07 ± 0.00 A	0.01 ± 0.00 A	0.02 ± 0.01 A	1.06 ± 0.04 A
	0.90≤ x<1.25	0.02 ± 0.01 A	0.02 ± 0.01 A	0.07 ± 0.01 A	0.01 ± 0.00 A	0.02 ± 0.00 A	1.07 ± 0.03 A
	x≥1.25	0.03 ± 0.01 A	0.02 ± 0.00 A	0.06 ± 0.01 A	0.01 ± 0.00 A	0.01 ± 0.00 A	1.10 ± 0.02 A
	Average	*0.03 ± 0.01 b*	*0.02 ± 0.00 b*	*0.07 ± 0.01 b*	*0.01 ± 0.00 a*	*0.02 ± 0.01 b*	*1.08 ± 0.02 a*
NIR-NT	x<0.90	0.05 ± 0.03 A	0.02 ± 0.00 A	0.06 ± 0.01 A	0.00 ± 0.00 A	0.02 ± 0.00 A	0.99 ± 0.08 A
	0.90≤x< 1.25	0.03 ± 0.01 A	0.02 ± 0.01 A	0.06 ± 0.02 A	0.01 ± 0.00 A	0.02 ± 0.01 A	1.01 ± 0.10 A
	x≥1.25	0.03 ± 0.01 A	0.01 ± 0.00 A	0.06 ± 0.01 A	0.00 ± 0.00 A	0.01 ± 0.01 A	1.01 ± 0.10 A
	Average	*0.04 ± 0.01 b*	*0.02 ± 0.01 b*	*0.06 ± 0.00 b*	*0.00 ± 0.01 a*	*0.02 ± 0.01 b*	*1.00 ± 0.01 a*
IRR-T	x<0.90	0.10 ± 0.03 A	0.11 ± 0.02 A	0.18 ± 0.04 A	0.04 ± 0.02 A	0.07 ± 0.05 A	1.08 ± 0.16 A
	0.90≤x<1.25	0.06 ± 0.02 B	0.02 ± 0.00 B	0.13 ± 0.01 A	0.01 ± 0.00 B	0.05 ± 0.02 B	1.08 ± 0.12 A
	x≥1.25	0.04 ± 0.01 B	0.04 ± 0.00 B	0.10 ± 0.02 B	0.01 ± 0.00 B	0.04 ± 0.02 B	0.78 ± 0.17 B
	Average	*0.07 ± 0.03 a*	*0.06 ± 0.05 a*	*0.14 ± 0.04 a*	*0.02 ± 0.02 a*	*0.05 ± 0.02 a*	*0.98 ± 0.17 a*
NIR-T	x<0.90	0.03 ± 0.01 A	0.02 ± 0.00 A	0.06 ± 0.01 A	0.00 ± 0.00 A	0.02 ± 0.00 A	1.06 ± 0.09 A
	0.90≤x<1.25	0.02 ± 0.01 A	0.02 ± 0.00 A	0.06 ± 0.01 A	0.01 ± 0.00 A	0.02 ± 0.01 A	1.03 ± 0.08 A
	x≥1.25	0.03 ± 0.00 A	0.01 ± 0.00 A	0.07 ± 0.01 A	0.01 ± 0.00 A	0.02 ± 0.01 A	1.08 ± 0.04 A
	Average	*0.03 ± 0.01 b*	*0.02 ± 0.01 b*	*0.06 ± 0.01 b*	*0.01 ± 0.01 a*	*0.02 ± 0.00 b*	*1.06 ± 0.03 a*

are undesirable in grapes, as during winemaking processes, they are partly transferred into the wine, where they can catalyze oxidative reactions, modify wine taste characteristics, and/or induce haziness. This negative phenomenon, called 'ferric and copper casse', is caused by the formation of an unstable colloid resulting from a reaction between Fe and Cu cations (Fe^{2+}, Fe^{3+}, Cu^{+} and Cu^{2+}), proteins and phosphoric acid. Furthermore, the perception of a negative metallic olfactory sensation is occasionally found in red wines, and it can be induced by Fe, Cu and Zn ions already present in the berries (Clarke and Bakker 2004). In addition, ferric iron reacts with anthocyanins, producing a soluble complex that leads to a too high color intensity (darker, more purplish hue), Cu has a detrimental effect as it can delay fermentation during winemaking, while Zn toxicity can affect root growth, and is occasionally associated with the use of contaminated compost (Jackson 2000). In red grapes and wines, Ca is involved in colloid flocculation and salt precipitation, being responsible for wine turbidity (Ribéreau-Gayon *et al.* 2006). Furthermore, Ca has a significant role in the resistance against *Botrytis cinerea* infection (Conde *et al.* 2007). In our experiment, no significant changes in Ca content were observed among the four treatments (Tab. 1), so confirming that reducing irrigation water does not represent a danger for wine quality. This could be due to the fact that Ca is a poorly soluble cation and it is not efficiently trasnslocated through the xylem (Ribéreau-Gayon *et al.* 2006, Conde *et al.* 2007).

In red wines, the small quantities of Mn (1-3 mg·L^{-1}) derive mainly from seeds (Jackson 2000) but our results also showed that this element is also present in the skin, where its levels were not affected by drought nor calcite (Tab. 2). Elements such as Pb, Hg, Cd, and Se are potentially toxic and, if present in the fruit, they usually precipi-

tate during fermentation (von Hellmuth *et al.* 1985). Thus, their occurrence in wine at above trace amounts usually indicates contamination after fermentation. In the case of Pb, Hg and Cd, the levels strongly increased in absence of irrigation, whereas the trend was reversed for Se (Tab. 2). The concentration of other microelements, such as As and Ni, usually present in grapes as metal sulfides was affected by drought (Tab. 2). The microelements normally found in grapevines grown under non-polluted sites, with the exception of the natural deposition of trace elements from the atmosphere (e.g. volcanic eruptions and in dust and sea spray), are normally derived from parent soils (White 2003). The difference here observed in the levels of some microelements demonstrated that also water availability and the amount of light absorbed by the berry have a key role in their regulation (Tab. 2).

Emphasis has been recently placed on the study of food and wine lanthanides distribution (Galgano *et al.* 2008, Volpe *et al.* 2009, Bentlin *et al.* 2011). These elements, though present at low concentrations ($\mu g \cdot L^{-1}$ to $ng \cdot L^{-1}$ level), arouse great interest for traceability studies because they could be significantly detectable in foods according to a distribution reflecting their presence in soils. Even if in 'Aglianico' berries, skin weight represents up to 27 % of total berry weight (Sofo *et al.* 2012) and decreasing lanthanides s gradient starting from roots to leaves, stems and flowers (Hu *et al.* 2004, Ding *et al.* 2006), our results demonstrated that skin lanthanide content was quite high (Tab. 3). This could be due to the fact that lanthanides are likely bound to chlorophyll during the previous photosynthetic activity of the berry (Hu *et al.* 2004). Among the lanthanides, the most abundant were Ce, La and Lu (Tab. 3), whereas Ce and La levels were the highest among the lanthanides both in berry skin and wine of a broad range of varieties (Galgano *et al.* 2008, Bertoldi *et al.* 2009). The high content of Lu here observed (approximately 1 $\mu g \cdot kg^{-1}$ dry berry skin) seems to be typical of 'Aglianico' (Tab. 3).

In conclusion, the results have highlighted that different irrigation managements and the exposition of the berry to light have resulted in quantitative changes of metals and metalloids in the skins. The dynamics of their extractability from grape berries to must during fermentation could be used to predict wine quality during the following processes and for wine traceability purposes. Such data can be of primary importance for understanding how grapevine responds in environments where water availability and light excess are by far the most important factors in quality control of grapes and wine.

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