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RESEARCH ARTICLE

Vitis vinifera L. variety Syrah sprayed with $ZnSO_4$: Effect on fruit quality and winemaking

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ABSTRACT

In grapevines, Zn is essential for normal leaf growth, shoot elongation and pollen development, allowing a fully developed berry. In this context, using as a test system *Vitis vinifera* L. variety Syrah, this study aimed to assess the interactions between Zn enrichment in grapes and sugars and fatty acids profiles, further considering the sensory implications of red wine production. Vineyard conditions of the soil were assessed to ensure the natural optimal development of grapevines and the workflow for Zn enrichment considered three treatments: foliar spray with water (control) and with $ZnSO_4$ (at 450 and 900g.ha^{-1}). After the 2nd foliar application of $ZnSO_4$, only minor changes of Zn, Ca and P contents were found in grapes (the levels of K, Cu and S increased significantly with $ZnSO_4$ (450 g.ha^{-1}). At harvest, the grapes submitted to foliar application of $ZnSO_4$ showed significantly higher levels of Zn (between 33.38 - 54.41%), but significant deviations in sugars (sucrose, glucose and fructose), fatty acids (C18:0, C18:1, C18:2, C18:3, C16:0, C<16:0) and color parameters were not found. After winemaking, relative to the control, a higher content of Zn persisted (60.59 - 63.82%), without impairing the characteristics desired by consumers. In fact, the wine with $ZnSO_4$ (900 g.ha^{-1}) was the most sensorially accepted.

Keywords: Foliar spraying with $ZnSO_4$; Grapes enrichment with Zn; Nutrient's interactions; Sugars and fatty acids profiles; *Vitis vinifera* L. variety Syrah; Winemaking

INTRODUCTION

Depending on body weight and phytate content in the diet, human organisms require an average daily intake of about 11 and 8 mg of Zn for adult males and females, respectively (Gammoh and Rink, 2017; IAEA, 2018). Below these Zn levels, the physiology of the human body can be affected, namely its physical development, the immune, reproductive and respiratory systems, skin properties and brain functions (Dapkekar et al., 2018; Sungaya et al., 2020; Younas et al., 2022). Zinc deficiency can result of poor food diets in diversity (one of the main reasons in developing countries), namely red meat, oysters, crab, nuts, and grain cereals (Dapkekar et al., 2018; Praharaj et al., 2021; Shkembi et al., 2021; Wang et al., 2018). Moreover, concerning cereal grains (a staple food worldwide), Zn contents are largely affected by their availability for root uptake since a great portion of the world's arable soils are deficient in this mineral (*ca.* 49 %). Zinc deficiency (*i.e.,* between 0.6 and 2.0 mg.kg^{-1}) commonly occurs in neutral and calcareous soils, intensively cropped soils, paddy soils and poorly drained soils, sodic and saline soils, peat soils, soils with high available phosphorus and silicon, sandy soils, highly weathered acid, and coarse-textured soils (Hacisalihoglu, 2020; Sungaya et al., 2020). Among the factors influencing Zn availability, pH, electrical conductivity, organic carbon

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and nutrient inter-actions are of great importance (Sungaya et al., 2020). Likewise, Zn is required in the range of 15 - 20 $mg.kg^{-1}_{DW}$ for optimal growth of crops (Marschner, 2012; Tsonev and Lidon, 2012), being its uptake and transport from roots to shoots (as Zn^{2+}) bound to organic acids (Hefferon, 2019; Sungaya et al., 2020). Moreover, decreased amounts of Zn lowers productivity and quality (Sungaya et al., 2020; Ullah et al., 2020), occurring specific symptoms that include visible growth changes in root, shoot, stem, seed, and fruit formation (Khan et al., 2022).

To surpass minerals deficiency in crops and comply with human needs in the diet, natural enrichment of minerals was emerged as a strategy to increase the accumulation of target nutrients (namely Zn) in the edible part of plants, namely the use of fertilizers through soil and/or foliar application (Bouis and Welch, 2010; Cakmak, 2008; Di Gioia et al., 2019; Hussain et al., 2022; Pal et al., 2019; Palmgren et al., 2008; Zulfiqar et al., 2020). Foliar spraying with Zn increases the content and yield of cereals and fruit trees (Nissar et al., 2019; Rugeles-Reyes et al., 2019). In this context, zinc sulfate is the most common used source and, additionally, also supplies crops with sulfur (*i.e.,* thus allowing Zn storing in the endosperm via S-rich proteins) (Szerement et al., 2022). Indeed, sulfur is also vital for plant growth, and its status further leads to implications for yield, quality, and plant response to abiotic stresses (Zenda et al., 2021). Besides, the positive effect of Zn fertilization on fruit may be due to its activity in tryptophan synthesis, cell division, maintenance of membrane structure and translocation of metabolites to the bud formation site, providing better fruit yield and quality (Zhang et al., 2013; Elsheery et al., 2020; Maity et al., 2023). Several studies in fruits (Subba et al., 2014; Rout and Sahoo, 2015; Song et al., 2015) also showed an increase in the concentration of phenolics (namely in grape berries) and anthocyanin content, that can be advantageous for the wine industry. Indeed, polyphenols are highly important phytochemicals promoting health benefits, whereas anthocyanins are responsible for the red color of wines (He et al., 2012; Onache et al., 2023).

Considering the case of viticulture an agro-food sector of great economic importance in Mediterranean climate zones (Gutiérrez-Gamboa et al., 2021; Tardaguila et al., 2011), that requires high grape standard for winemaking, soil nutrients can also limit growth and fruit quality (Lazcano et al., 2020; Zhao et al., 2019). In this context, using as a test system the winegrape *Vitis vinifera* L. variety (cv. Syrah), this study aimed to assess the interactions between Zn enrichment in grapes and some nutritional patterns (sugars and fatty acids profiles), further considering the implications on red wine production following consumers expectations.

MATERIALS AND METHODS

Experimental field

Under irrigation conditions, *Vitis vinifera* variety Syrah from a vineyard located in Setúbal, Portugal (Fig. 1, 38º 35'23.629"N; 8º 51' 46.208" W) was submitted to three leaf sprays with $ZnSO_4$ (at concentrations of 450 and 900 g. ha^{-1}, with control vines sprayed with water) after flowering, during the production cycle. During the cycle of the culture, temperatures reached maximum and minimum average values of 28 °C and 16.6 °C, respectively.

Soil analysis

Vineyard soils (28 samples (100 g) were collected from the soil surface and from a depth of 30 cm) were sieved (2.0 mm mesh to remove stones, coarse materials and other debris) and dried at 105 °C for 24 h, followed by a 1 h desiccation. Dry mass was then recorded and to quantity the organic matter, samples were also heated (to 550 °C, for 4 h, until a constant weight) and therefore desiccated until room temperature. Electrical conductivity and pH were performed, using a potentiometer (Luís et al., 2021). Mineral analysis was carried out with a XRF analyzer (model XL3t 950 He GOLDD+), under a helium atmosphere (Ni-ton Thermal Scientific, Munich, Germany) (Luís et al., 2021).

After heating the samples at 550°C for 4h, colorimetric parameters of soils were measured using a fixed wavelength according to (Marques et al., 2023). The illuminant D_{65}, the system of the Commission Internationale d'Éclaire (CIE) was applied. Brightness/brightness (L) and chromaticity parameters (a* and b* coordinates) were obtained with a Minolta CR 300 colorimeter (Minolta Corp., Ramsey, NJ, USA) coupled to a sample vessel (CR-A504). Parameter L* translates the variation of the tonality between dark and light, with a range between 0 (black) and 100 (white) and

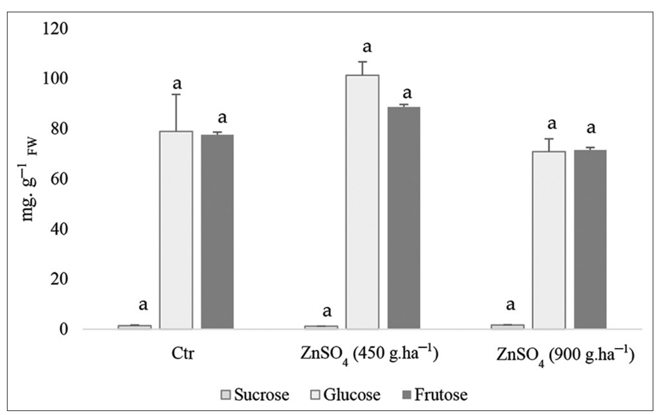

Fig 1. Mean values ± S.E. (n = 3) of sugar content (mg/g per fresh weight) in grapes of *Vitis vinifera* variety Syrah, at harvest. Letter a indicate the absence of significant differences among the treatments (statistical analysis using the single-factor ANOVA test, $p \leq 0.05$). Ctr: control samples.

a* and b* indicating color variations between red (+60) and green (-60), and between yellow (+60) and blue (-60), respectively.

Nutrients content in grapes

After the 2nd foliar application, and at harvest, samples of randomized grapes of *Vitis vinifera*, variety Syrah, were dried at 60 ºC (until constant weight), grounded and processed into pellets. Measurements were performed using an XRF analyzer (Thermo Scientific, Niton model XL3t 950 He GOLDD+, Waltham, MA, USA) under He atmos-phere (Pessoa et al., 2021).

Color parameters of grapes

At harvest, colorimetric parameters were determined in the pulp of randomized fresh grapes (n = 3 per treatment), with a scanning spectrophotometric colorimeter (Agrosta, European Union). The sensor provides a 40 nm full-width half-max detection, covering the visible region of the electromagnetic spectrum. This sensor has 6 phototransistors with sensibility in a specific region of the spectrum (380 nm—violet; 450 nm—blue; 500 nm—green; 570 nm—yellow; 600 nm—orange; 670 nm—red). Light was furnished by a white light-emitting diode (LED) covering all the visible regions as mentioned (Pessoa et al., 2022).

Sugars content in grapes at harvest

Sugar analyzes, using 40 g of pulp (removed from grape berries at harvest) per sample (n = 3), were carried out following (Daccak et al., 2022). After filtration (nylon 0.45 mm) samples were injected (40 μL) in an HPLC (Waters, Milford, MA, USA) system, coupled to a refractometric detector (Waters 2414), equipped with a SugarPak 1 column (Waters 6.5 _ 300 mm) and pre-column (Wat 088141) with SugarPak II inserts (Wat 015209). Ul-trapure water containing 50 ppm calcium EDTA was used as mobile phase, at a flow rate of 0.5 mL min^{-1}. Data were analyzed with Breeze software and quantified using calibration curves of sucrose, glucose, and fructose.

Fatty acids contents in grapes at harvest

Samples of three to four bunches composed of several berries without peduncle (ca. 5 g fresh weight) per treatment (3 replicates), were used for fatty acids (FAs) analyses following (Vidigal et al., 2018), through direct acidic transesterification using a methanol: sulfuric acid solution (39:1, v: v), after addition of an internal standard (heptadecanoic acid). Samples were thereafter analyzed by gas–liquid chromatograph (Varian CP-3380, Palo Alto, CA, USA), coupled to a flame ionization detector (GC-FID), and separated using a Varian capillary column (CP-Wax 52 CB). Double bond index (DBI) reflects the relative abundance of mono and polyunsaturated FAs relatively to saturated FAs, and was calculated using the formula: DBI = ((% monoenes + 2 _ % dienes + 3 _ % trienes)/% AG saturated) (Mazliak, 1983).

Winemaking and zinc quantification

The first phase of winemaking comprised destemming and pressing grapes (50 Kg), being therefore, sulfur dioxide was added (18 mL). After 24 h rest at 6 ºC, Springarom (18 g) was added to the vat and afterward (20 min), the yeast (hydrated with water at 37°C, (1:10)) was added. During all the process, temperature and density of the mixture were regularly measured, with PVPP/ Polyvinylpolypyrrolidone—Divergan F (12 g) application when density reached 1060 $g.cm^{-3}$. Besides, DAP—Diammonium phosphate (12 g) was further added at the peak of fermentation (density between 1030–1040 $g.cm^{-3}$) and when the density reached 1000 $g.cm^{-3}$. Additionally, sulfur dioxide (3 mL) was applied when the density reached 990 $g.cm^{-3}$. The wine was then filtered, followed by bottling. Measurements of Zn of grapes samples and wine were analyzed by atomic absorption spectrophotometry using a Perkin Elmer AAnalyst 200 (Waltham, MA, USA), fitted with a deuterium background corrector, and using the AA WinLab software program, as described by (Daccak et al., 2022).

Sensory analysis of the wine was performed with a semi-trained panel of tasters (n = 14) with 5 women and 9 men, aged 44-63 and 30-64, respectively. Based on a preset 5-point hedonic scale, varying gradually from "I greatly disliked" to "I liked it a lot", where tasters classify sensory attributes (persistence, sweetness, effervescence, bitterness and acidity) and also performed a global evaluation.

Statistical analysis

Data were statistically analyzed using a one-way ANOVA to assess differences between treatments, followed by a Tukey's test for mean comparison. Letters a, b indicates significant differences among treatments. A 95% confidence level was adopted for all tests.

RESULTS

The soil of the vineyard showed a slightly acidity (pH of 6.51) and an electrical conductivity, organic matter and moisture of 186 $\mu S.cm^{-1}$, 3.14 % and 8.04 %, respectively (Table 1). In this context, nutrients contents displayed (Table 1) the following pattern Fe > K > Ca > P> Mg > Mn > S > Zn > Cu, whereas after organic matter removal, the color parameters a* and b* showed (Table 1) a greater contribution of red and yellow (ranging between

Table 1: Characterization of soil (0–30 cm deep) in the tested vineyard (n=28 for quantification of chemical elements and colorimetric soil analysis)

pH	Soil analysis (0-30 cm deep) (n=28)										
	Electrical Conductivity	Organic Matter	Ca	K	Mg	P	Fe	S	Zn	Mn	Cu
	µS.cm^{-1}	%					ppm				
6.51 ± 0.06	186 ± 14.61	3.14 ± 0.11	0.24 ± 0.03	1.34 ± 0.02	0.07 ± 0.00	0.12 ± 0.01	2.27 ± 0.15	49.7 ± 2.50	36.3 ± 3.99	154 ± 9.06	32.7 ± 3.00

Colorimetric Soil analysis (0-30 cm deep) (n=28)					
With organic matter			Without organic matter		
L	a*	b*	L	a*	b
45.72 ± 0.36	7.58 ± 0.23	24.11 ± 0.36	45.78 ± 0.52	21.42 ± 0.18	31.10 ± 0.36

45.72-45.78 for L, 7.58- 21.42 for a* and 24.11- 31.10 for b* - Table 1).

After the 2nd foliar application of $ZnSO_4$, relative to the control, the contents of Zn in the Syrah grapes did not vary significantly (although displaying a slight increase of 1.05 and 1.03 fold, to values of 31.85 and 31.22 mg.kg^{-1} after application of 450 and 900 g.ha^{-1} - Table 2). Among treatments, the levels of Ca and P also did not vary significantly and ranged between 0.87 - 1.05% and 0.35- 0.45 %, respectively. Moreover, the contents of K increased from the control onwards (varying between 2.44 - 3.50 %, whereas Cu and S revealed the highest value after pulverization with 450 g.ha^{-1}, ranging between 32.85- 59.59 and 0.31- 0.40% mg.kg^{-1}, respectively) (Table 2). At harvest, relatively to the control, grapes sprayed with $ZnSO_4$ revealed significantly higher contents of Zn (1.54 and 1.33 fold for treatments with 450 and 900 g.ha^{-1} - Table 2).

The contents of sucrose, glucose, and fructose in the pulp of Syrah grapes did not show significant differences among treatments (Fig. 1). The amounts of glucose prevailed (with values varying between 70.88 - 101.33 %), followed by fructose (with proportions ranging between 71.49 - 88.71%) and sucrose (with its levels changing between 1.28 - 1.73%) (Fig. 1). Interesting was to note that grapes treated with 450 g.ha^{-1}, revealed the highest amount of these sugars (Fig. 1).

At harvest, the fatty acids (FAs) profile of the grapes showed the following relative abundance: (C18:2) > (C18:3)> (C16:0) > (C18:0) > (C18:1) > chains inferior to 16 C (<16:0) (Table 3). Relatively to the control, each FA of all treated grapes did not reveal (Table 3) any significant variation (except C18:3 which showed significantly higher values in grapes treated with 450 g.ha^{-1}). Besides, significant deviations could not be found among treatments (Table 3) for total fatty acid content (TFA) and the degree of unsaturation (DBI).

In the visible spectral region (450–650 nm) colorimetric parameters of harvested grapes also didn't show (Table 4; Fig. 2) significant differences among treatments (except at 500 nm, with the control showing a lower value).

After winemaking, the amount of Zn remained significantly higher in $ZnSO_4$-sprayed grapes relative to the control (60.59% and 63.82 % higher from grapes treated with 900 and 450 g.ha^{-1}, respectively - Fig. 3).

Sensory analysis of Syrah red wine showed a correlation of $ZnSO_4$ application with increased acidity and persistence and decreased sweetness (Fig. 4- A). Besides, some sensory

Table 2: Mean values ± S.E. (n=3) of nutrients concentration (Zn and Cu in $mg.kg^{-1}$ and Ca, K, S and P in %) in grapes of *Vitis vinifera* variety Syrah after the 2nd foliar application of $ZnSO_4$ and at harvest. Letters a, b indicates significant differences among the treatments (statistical analysis using the single-factor ANOVA test, P ≤ 0.05). Ctr: control samples

Cv. Syrah Nutrient Content							
	After 2nd foliar application						At harvest
Samples	Ca	K	S	P	Cu	Zn	Zn
	(%)				(mg.kg⁻¹)		
Ctr	0.87 ± 0.10[a]	2.44 ± 0.01[b]	0.31 ± 0.02[b]	0.35 ± 0.04[a]	33.71 ± 4.0[b]	30.24 ± 0.94[a]	7.94 ± 0.41[b]
$ZnSO_4$ (450 g.ha⁻¹)	1.04 ± 0.03[a]	3.50 ± 0.26[a]	0.40 ± 0.01[a]	0.45 ± 0.02[a]	59.59 ± 2.11[a]	31.85 ± 1.18[a]	12.26 ± 0.67[a]
$ZnSO_4$ (900 g.ha⁻¹)	1.00 ± 0.03[a]	2.52 ± 0.16[b]	0.35 ± 0.01[b]	0.43 ± 0.01[a]	32.85 ± 3.20[b]	31.22 ± 0.86[a]	10.59 ± 1.19[ab]

Table 3: Mean values ± S.E. (n=3) of fatty acid profile (mol %), total fatty acid content (TEA) and unsaturation (DBI, double bond index) of grapes from *Vitis vinifera* variety Syrah, at harvest. Linoleic acid (C18:2), linolenic acid (C18:3), palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and chains inferior to 16 C (<16:0). Letters a, b indicates significant differences among the treatments (statistical analysis using the single-factor ANOVA test, P ≤ 0.05). Ctr: control samples

Treatments	Cv. Syrah							
	Fatty acids						TFA	DBI
	<C16:0	C16:0	C18:0	C18:1	C18:2	C18:3		
Ctr	0.28 ± 0.03[a]	15.36 ± 3.43[a]	14.42 ± 3.55[a]	8.17 ± 0.41[a]	37.41 ± 1.35[a]	24.36 ± 0.83[ab]	1.02 ± 0.20[a]	5.20 ± 0.19[a]
$ZnSO_4$ (450 g.ha⁻¹)	0.57 ± 0.16[a]	19.11 ± 1.09[a]	6.21 ± 0.32[a]	7.85 ± 0.66[a]	37.40 ± 0.54[a]	28.87 ± 1.29[a]	1.28 ± 0.10[a]	6.57 ± 0.38[a]
$ZnSO_4$ (900 g.ha⁻¹)	0.17 ± 0.03[a]	17.95 ± 1.52[a]	12.12 ± 3.35[a]	7.69 ± 1.00[a]	38.55 ± 3.84[a]	23.52 ± 1.24[b]	0.77 ± 0.15[a]	5.51 ± 1.16[a]

Table 4: Mean values ± S.E. (n=3) of the transmittance of visible spectra in grapes of *Vitis vinifera* cv. Syrah, at harvest. Letters a, b indicate significant differences among the treatments (statistical analysis using the single-factor ANOVA test, P ≤ 0.05). Ctr: control samples

Cv. Syrah Transmittance (nm)						
Treatments	450	500	550	570	600	650
Ctr	520 ± 17[a]	374 ± 19b	427 ± 71[a]	243 ± 22[a]	326 ± 31[a]	760 ± 18[a]
$ZnSO_4$ (450 g.ha⁻¹)	528 ± 5[a]	393 ± 12[a]b	560 ± 66[a]	277 ± 24[a]	360 ± 24[a]	755 ± 6[a]
$ZnSO_4$ (900 g.ha⁻¹)	564 ± 8[a]	430 ± 6[a]	633 ± 17[a]	315 ± 4[a]	400 ± 2[a]	778 ± 8[a]

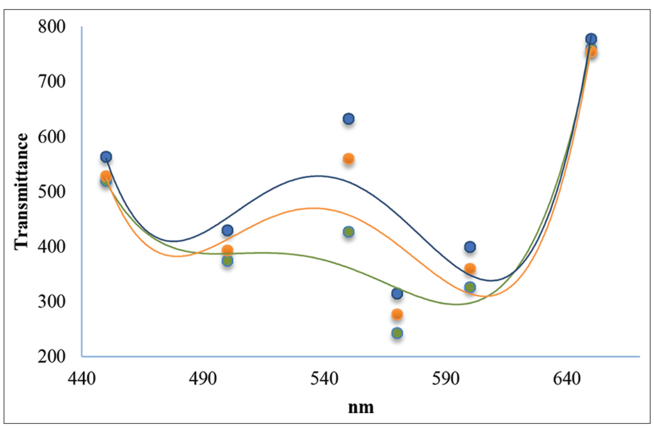

Fig 2. Visible spectra with the mean values of transmittance in grapes of *Vitis vinifera* variety Syrah, at harvest. Ctr: control samples. Ctr (●); $ZnSO_4$ 400 g.ha⁻¹ (●); $ZnSO_4$ 900 g.ha⁻¹ (●).

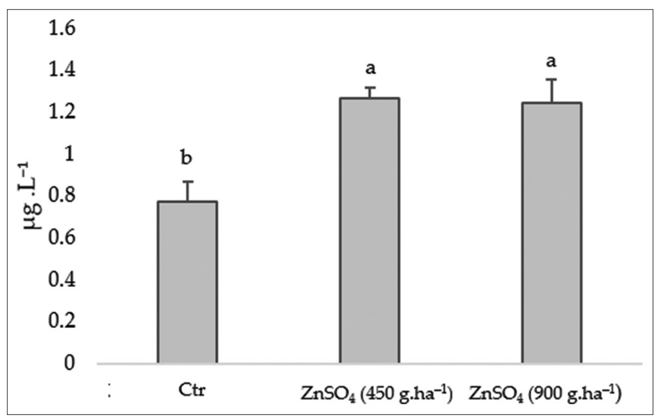

Fig 3. Mean ± S.E. (n = 3) of Zn concentrations in wine of *Vitis vinifera* variety Syrah produced with the grapes sprayed with $ZnSO_4$ at concentrations of 450 and 900 g.ha⁻¹. Letters a, b indicates significant differences among the treatments (statistical analysis using the single factor ANOVA test, P <0.05). Ctr: control samples.

parameters showed several variations, namely bitterness and effervescence but a clear trend was not found (Fig. 4- A). Nevertheless, the tasters showed a greater appreciation for the wine produced with grapes treated with $ZnSO_4$ (900 g. ha⁻¹), indicating a high maintenance of acceptability (Fig. 4- B).

DISCUSSION

It is well known that grapevines can grow in different soil types if an adequate nutrient supply and water availability for good development is provide (Comino et al., 2017;

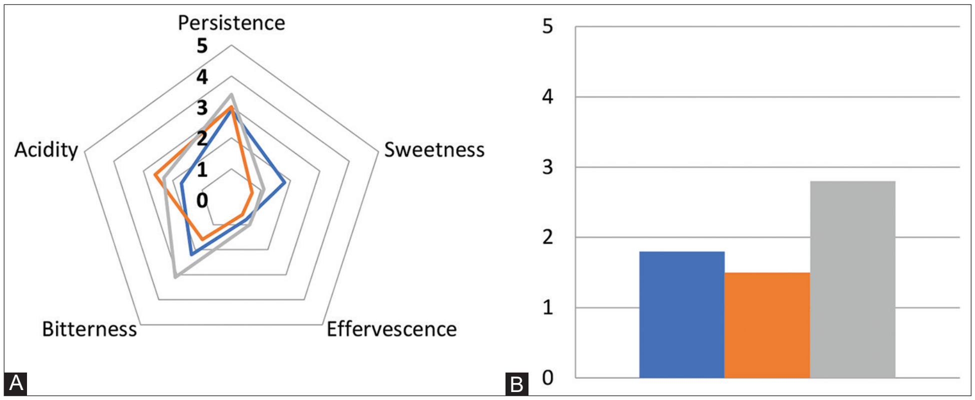

Fig 4. Mean values (n = 14) of sensory analysis of wine *Vitis vinifera* variety Syrah produced with the grapes sprayed with $ZnSO_4$ at concentrations of 450 and 900 g.ha^{-1}. Ctr: control samples. (A) Sensory attributes (Persistence, sweetness, effervescence, bitterness and acidity) (Ctr (▬); $ZnSO_4$ (400 g.ha^{-1})(▬); $ZnSO_4$ (900 g.ha^{-1}) (▬)) and (B) Global evaluation (Ctr (■); $ZnSO_4$ (400 g.ha^{-1})(■); $ZnSO_4$ (900 g.ha^{-1}) (■)).

Shahane and Shivay, 2021). Yet, bioavailability for minerals uptake depends on several factors, such as organic matter, electrical conductivity, pH, water content and temperature (Bravo et al., 2017; Kotsaki et al., 2020), that can affect wine quality (Leeuwen et al., 2018). In fact, organic matter deficiency is a common issue in the viticulture sector (especially in Mediterranean climate, since low contents prevails - usually about 0.5- 1.0%), however in the soil of the tested vineyard a higher content was found (3.14 %) (Table 1), which can be consider within the ideal range for crop productivity (Cataldo et al., 2021; Olego et al., 2022; Tangolar et al., 2020). Besides, at a depth of 30 cm, the electric conductivity of the soil from the vineyard was 186 µs.cm^{-1} (Table 1), which was within the common ranges for high productivity, namely under irrigation (Ozpinar et al., 2018; Yu and Kurtural, 2020), as it determined the relation between higher salt content and greater energy expenditure for water absorption by roots. A slightly acid pH (6.51) was also found (Table 1) in the vineyard, which can be consider optimal for nutrient uptake as it remains within the range of 5.5 - 8 (Longbottom, 2009). Additionally, the contents of nutrients in the soil also were found to be adequate (Table 1), as remained similar to those from other vineyards that have a high-quality production of grapes, namely for Ca, Mg and Fe (Catarino et al., 2018), Zn, Mn, Cu and K (Richardson and Chase, 2021) and S and P. (Haylin et al., 2012). Interesting was to note that, as previously found (Margesin and Schinner, 2005), after the removal of organic matter, the colorimetric parameters a* and b* increased, indicating a high pigmenting power of iron oxides (as parameter a* depends mainly on the content of sesquioxide and non-hydrated iron oxides, and parameter b* is linked to the content of hydrated oxides). Globally, all soil parameters of the vineyard indicated that grapevines were submitted to optimal conditions, being adequate for testing the interactions between grapes enrichment with Zn (through foliar spraying) and accumulation of other nutrients, as well as the implications on sugars and fatty acids that largely determine winemaking.

It is well known that, in different crops, increasing levels of Zn trigger antagonistic interactions with the accumulation of P, Ca and Cu (Mousavi et al., 2012; Prasad et al., 2016; René et al., 2017), yet after the 2nd foliar spraying with $ZnSO_4$ at 450 and 900 g.ha^{-1} these trends could not be detected in grapes, as Zn levels did not vary significantly (Table 2). In this context it was also reported that in crops Zn can display synergistic interactions with K and S (Das and Green, 2016; Prasad et al., 2016), but after the 2nd foliar spraying, although Zn contents did not vary significantly, the slightly higher amount of this nutrient in Zn-treated grapevines with 450 g. ha^{-1}, suggest a higher uptake rate resulting of additional membrane permeability. Moreover, at harvest the contents of Zn increased significantly (Table 2) after foliar application of $ZnSO_4$ to the grapevines (between *ca.* 33.38 – 54.41%), therefore displaying a similar trend to these previously found with other crops (about 25 - 63% Zn enrichment) (Cakmak and Kutman, 2018; De Valença et al., 2017).

The color of wines is one of the attributes most appreciated by consumers, especially in red wines, being dependent on the anthocyanin concentration and composition in the grapes, which changes as they undergo chemical reactions (*i.e.*, degradation, oxidation, aggregation and precipitation with other macromolecular compounds) (Zhao et al., 2022). At harvest, colorimetric parameters of grapes did not reveal significant variations (except at 500 nm, with $ZnSO_4$ 900 g.ha^{-1}, presenting a higher value relative to the control), therefore, in general, indicating the absence of negative impacts of $ZnSO_4$ application (Table 4; Fig. 2).

Foliar spraying with $ZnSO_4$, although triggering higher contents of Zn in grapes (Table 2), did not significantly affect the levels of sucrose, glucose and fructose among treatments. Still the lowest levels were found for sucrose

(Fig. 1) mostly due to its hydrolysis. Accordingly, these data pointed that higher accumulation of Zn in grapes did not affect the synthesis of organic acids and phenolics, alcohol concentration in wines and aroma compounds (Trad et al., 2017; Walker et al., 2021; Zhang, 2021) and, therefore, any impact on quality. Although the composition of fatty acids might vary with ripening conditions, grape variety, year of harvest and geographical location (Kapcsándi et al., 2021; Szabó et al., 2021), total fatty acids (usually about 90% of fatty acids mono- and polysaturated (Kapcsándi et al., 2021; Sabra et al., 2021) and their relative composition, as well as the extend of unsaturation, did not vary significantly (except the contents of C18:3), further indicating the absence of interactions with Zn enrichment in the grapes (Table 3). This result is relevant because it shows the maintenance of essential cellular solutes and the normal functioning of various metabolic processes (Brizzolara et al., 2020). Indeed, fatty acids composition remained similar to these found in other grapes varieties (Kapcsándi et al., 2021; Sabra et al., 2021; Vašeková et al., 2020), but the higher levels of C18:3 in treatment 450 $g.ha^{-1}$ can favor winemaking, as they are precursors of alcohols, aldehydes and thiols that are essentials for herbaceous aromas and tropical notes (Pérez-Navarro et al., 2019). In fact, the application of $ZnSO_4$ showed no depreciative changes for the wine, as observed in the sensory analyses (Fig. 4). Additionally, although the winemaking process can affect the mineral composition of wines (De Valença et al., 2017; Shimizu et al., 2020), relative to the control, the amounts of Zn also remained higher (*ca*. 60.59 – 63.82% - Fig. 3), which might contribute if moderately consumed to prevention of some diseases (Santos et al., 2011; Szabó et al., 2021).

CONCLUSION

Grapes from the Syrah cultivar submitted to foliar spraying with $ZnSO_4$, at 450 and 900 $g.ha^{-1}$, were effective to increase Zn contents, without negative effects on sugars (sucrose, glucose and fructose), fatty acids (C18:0, C18:1, C18:2, C18:3, C16:0, C<16:0) and color parameters. After winemaking, Zn enrichment persisted in the red wine, keeping high quality due to the general maintenance of sugars and acyl lipids composition and without depreciative changes at a sensory level. Further studies with other varieties and complimentary quality analyses are still required for the characterization of enriched grapes with zinc, namely following a metabolic perspective and for further development of winemaking.

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Author contributions

All authors contributed equally to the research and discussion of the obtained data of the manuscript. Additionally, all authors further contributed to the writing of the different sections of the paper.

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