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# Zn nutrition of Vitis Vinifera White Grapes: Characterization of Antagonistic and Synergistic Interactions by $\mu$ EDXRF tissue analyses

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Abstract: Nutritional status performs an essential role in agriculture, affecting productivity and keeping crops functioning properly. Despite being required in smaller amounts, micronutrients are also needed for adequate growth, namely Zn (zinc) with regulatory, catalytic and structural functions. Fertilization with Zn is used to ameliorate the deficits of this micronutrient in more susceptible crops such as grapes. Yet, the management of this application must consider the antagonistic and synergistic interactions among nutrients, as it affects their uptake and translocation rates. Therefore, a workflow with three ZnO foliar applications (30 % and 60 %, 450 and 900 g ha<sup>-1</sup> respectively) in the variety Vitis Vinifera cv. Fernão Pires, was implemented in a field located in Palmela, Portugal. The concentration of Zn in the tissues was therefore evaluated by microenergy X-ray dispersion fluorescence (µEDXRF), showing an increase of 1.82 and 2.54 times in the seed and skin of grapes fertilized with a concentration of 60 %, compared to control grapes, respectively. Using the same method, a synergistic relationship was observed for macronutrients such as Ca and K, and micronutrients such as Fe, P and Mn. In addition, a complementary analysis of grapes' density was carried out to verify changes in quality, in which no negative impact was observed due to Zn application. This study allows us to verify that the concentration of the applied Zn fertilizer brings benefits in the amount of nutrients that are important for development and crops quality.

Keywords: antagonism; grapes; synergism; Vitis vinifera; Zn fertilizer.

# Introduction

Micronutrient's deficiencies or hidden hunger is affecting more than 2 billion people worldwide, leading to the development of strategies to mitigate this problem (Gödecke et al., 2018). Fertilizing fruit trees, namely the vineyard, is considered an important tool to meet nutritional needs and optimize the yield and quality of the grapes (Brunetto et al., 2015; Song et al., 2015).

Zinc (Zn) deficits are common worldwide, affecting the vine (Sabir and Sari, 2019) and is important for plant growth, with catalytic, structural and regulatory functions (Jurowski et al., 2014), as a co-factor in the auxin metabolism, enzymatic activation, chlorophyll and nucleotide synthesis, and genes expression and regulation (Luís et al., 2021). According to research in grapefruit, Zn agronomic biofortification has been shown to be efficient and, in addition enhancing growth and development (Fu et al., 2016).

Likewise, phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulphur (S), iron (Fe) and manganese (Mn) are also essential, affecting crops productivity (Toor et al., 2021). Yet, through application of one nutrient, absorption and utilization of other nutrients can be affected, in a positive or negative way, in a synergistic and antagonistic relationship respectively (Palani and Raju, 2019).

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# **Results and Discussion**

#### Table 1

Table 2

Micronutrient (Seed)						Macronutrient (Seed)			
Sample	Zn	Fe	Mn	Р		Sample	Ca	K	Mg
Control	$24.6 \pm 1.23 c$	$91.6 \pm 4.58a$	$8.22\pm0.41c$	$0.00 \pm 0.00c$	-	Control	$0.82\pm0.04c$	$6.11 \pm 0.31 ab$	$12.4 \pm 0.62a$
ZnO 30 %	$37.1 \pm 1.85 b$	106 ± 5.31a	$14.8\pm0.74b$	$1148\pm57.4b$	-	ZnO 30 %	2.98 ± 0.15a	$6.40 \pm 0.32a$	$0.39 \pm 0.02c$
ZnO 60 %	$44.7\pm2.24a$	$105 \pm 5.24a$	$35.9 \pm 1.79a$	$3403 \pm 170a$	-	ZnO 60 %	$1.88 \pm 0.09b$	$5.16 \pm 0.26b$	$2.78 \pm 0.14b$
Micronutrients (Flesh)						Macronutrients (Flesh)			
Control	$23.4\pm1.17b$	$91.2\pm4.56c$	$8.66\pm0.43c$	$0.00 \pm 0.00c$	-	Control	$0.35 \pm 0.02c$	$5.44 \pm 0.27c$	$10.0 \pm 0.50a$
ZnO 30 %	$54.4\pm2.72a$	$278 \pm 13.9a$	$27.4 \pm 1.37 b$	$2662 \pm 133a$	-	ZnO 30 %	$1.89 \pm 0.09a$	$15.4 \pm 0.77a$	$5.84 \pm 0.29b$
ZnO 60 %	$59.4 \pm 2.97 a$	$228 \pm 11.4b$	$51.8 \pm 2.59a$	$2203 \pm 110b$	-	ZnO 60 %	$1.24\pm0.06b$	$10.9 \pm 0.55b$	$5.51\pm0.28b$
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- Foliar applications with ZnO at different concentrations (i.e, 450 and 900 g ha-1) in vines, prove to be efficient in increasing the Zn content in grapes (2.54 times more in the flesh and 1.82 in seed) (Table 1);
- Other nutrients accessed, showed mainly an interaction of synergism in the case of micronutrients and macronutrients such as P, Mn, Ca, Fe and K (except Mg) (Table 1 and 2);
- The results obtained, showed that increase of Zn concentration, enhanced the uptake of other nutrients, suggesting that micronutrients as Zn stimulate the plant metabolism resulting in an intensified uptake of nutrients through the roots (Stepien and Wojtkowiak, 2016). Also, Zn fertilization is related to positive effects on photosynthesis and chlorophyll synthesis, which also facilitates the absorption and accumulation of nutrients in the leaves (Xie et al., 2020);
- As for the antagonistic interactions, in this study, they only occurred in Mg, where the greatest amount of treatment with Zn significantly reduced the Mg concentration.

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# **Results and Discussion**



- According to literature, higher densities (*i.e.*, ≥ 1088 kg m<sup>-3</sup>) demonstrated benefits, being more advantageous for health and sensorially (Rolle et al., 2015);
- Fernão Pires grapes presented greater values ranging between 1150 2185 kg m<sup>-3</sup>, where fertilization didn't negatively affect the quality of grapes;
- Fertilized grapes showed higher values than control, although not significant.

### Conclusions

Zinc foliar fertilization with ZnO is efficient, increasing the amount of this micronutrient in the flesh and seeds of the grape cv. Fernão Pires, and presenting a synergistic relationship with P, Fe, Mn, Ca and K. Thus, this technique is an important tool to improve the nutritional status and quality of the grape. An antagonistic relationship with the macronutrient Mg was also observed. Additionally, fertilization did not affect density, with Fernão Pires grapes presenting values greater than 1088 kg m<sup>-3</sup> being important for health and sensory.



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