



Mineral composition of organic and conventional white wines from Italy

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ABSTRACT

Despite of the increased interest of consumers for organic agro-food products and of the growing demand for organic wines, scientific literature reports a limited number of studies aimed to evaluate the chemical composition of organic wine with respect to conventional wine in terms of major and trace metals. In the present study the concentrations of 19 elements (Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn) were determined in samples of white wines from Italy, conventionally and organically produced. No significant difference in the mineral composition was found between the two groups, except for Ni, which showed a higher concentration in organic wines. By comparing our data with data from literature it can be pointed out that there is no agreement among the results presented in the different studies referring to comparisons between organically and conventionally produced wines, concluding that the mineral composition of wines depends on factors different from organic/conventional production method.

1. Introduction

Italy is the first wine producing country in the world, with a production of 48.5 million hL in 2018, and it is the second country for exports, both in terms of volume (21.4 million hL) and in terms of value (5.9 billion euro) (EC, 2019; OIV, 2018).

Considering that wine is the leading product of exports among the Italian agri-food products, it is challenging to respond to consumer expectations in terms of quality, safety and sustainability. During the last years the growing concern about health and environmental issues has led to an increased demand for organic wines, as shown by a fast growth of this sector in terms of market volume and of hectares of organic vineyards. Currently 73% of all organic vineyard in the world are located in three European countries, Spain, Italy and France, and it is expected that organic wine production will continue to grow in the next years (EC, 2018).

In the scientific literature several studies have been performed with the objective of comparing organic and conventional wines in terms of chemical composition, however the vast majority deals with differences in the content of antioxidant compounds, polyphenols, anthocyanins, biogenic amines and pesticides (Garaguso and Nardini, 2015; Mulero et al., 2009, 2010; Patrignani et al., 2017; Tassoni et al., 2013). The mineral constituents have been investigated in a limited number of studies and there are no convincing results regarding major and trace elements in organic with respect to conventional wine (Čepo et al., 2018; Dutra et al., 2018; Koreňowská and Suhaj, 2012; Vrček et al., 2011; Tobolková et al., 2014).

Trace metals in wines are due to many factors, related to the specific production area, such as grape variety, soil and climate, cultivation, yeast, wine-making practices, transport and storage. Moreover, trace elements can enter the product through raw materials, as additional ingredients during the winemaking practice, or as impurities from the contact with the process equipment itself in the different phases of the oenological process, including aging and storage (Ibanez et al., 2008; Pohl, 2007; Vázquez et al., 2013; Volpe et al., 2009).

Considering the relevance of metals in food quality and safety (Tariba, 2011), the present study aims to increase the knowledge about the composition of organic and conventional wines. Even if this issue has already been studied by some Authors, the possibility of confirming or contradicting what is reported in literature in previous studies is a central aspect of scientific research, although often considered of minor importance.

The metal content of red wines is very different from that of white wines (Cabrita et al., 2018; Mirabal-Gallardo et al., 2018; Minganti and Drava, unpublished data); for this reason the present study was limited to white wines only.

2. Materials and methods

2.1. Sampling

A total of 23 samples of wine representing the most popular white wine varieties (e.g. Chardonnay, Prosecco, Müller-Thurgau, Pinot grigio)

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of Northern and Central Italy were collected in the local market during 2018. Where possible, for each wine from a certain region, a sample of conventionally produced ($n = 12$) and a sample of organically produced wines ($n = 11$), as certified by the presence of the EU-organic-logo and the code number of the certifier on the label according the current European regulation (EU, 2012), were analyzed.

2.2. Analytical procedure

The concentrations of 19 elements (Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn) were measured using atomic emission spectrometry with an inductively coupled plasma source (ICP-OES) using an iCAP 7000 Series (Thermo Scientific, UK) with axial plasma view for a better sensitivity for Al, As, B, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, V and Zn, and with radial view for Ca, K, Mg and Na.

The reagents used were: Type I water ($>18 \text{ M}\Omega \text{ cm}$; Puraniti TU3+, VWR International bvba, Belgium), 65% (m/m) nitric acid ("for trace analysis", Scharlau Chemie SA, Spain), 1000 $\mu\text{g/mL}$ or 10000 $\mu\text{g/mL}$ single ICP Standard Solutions (VWR International LLC, USA), and ethanol 96% Reagent Grade (Scharlau Chemie SA, Spain). All glassware was soaked (24 h) in 3 M nitric acid and rinsed with Type I water.

The wines were filtered with a 0.45 μm nylon filter (VWR International LLC, USA) and analyzed without any other treatment than the dilution. For the trace elements (Al, As, B, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr, V and Zn) the sample was diluted 2.5 times, while for the major elements (Ca, K, Mg, and Na) the dilution was 10 times. ICP-OES analysis without any sample mineralization is a practice commonly used in wine analysis and provides results comparable to those obtained with the more complex acid digestion (Pérez-Álvarez et al., 2019; Thiel et al., 2004). ICP-OES was operated at 1150 W with a gas (Ar) flow of 12 L/min and an auxiliary flow of 0.5 L/min. Sample (0.630 mL/min) was introduced via a glass concentric nebulizer mounted on a cyclonic spray chamber. Calibration was carried out with standards prepared using the wine matrix in a procedure similar to the standard addition method, in order to have solutions with a matrix which really matches the real solutions. Standard solutions were added in order to match the natural concentration of each trace element in wine. A three-point calibration was used. A blank (10% by volume ethanol) was treated and analyzed as the sample, and subtracted from all measurements. Except for the elements close to their detection limit, all other measurements showed a good reproducibility, with a mean coefficient of variation ($n = 5$) ranging from 1% (for Mn) to 6% (for Zn). Consequently, all samples were analyzed in duplicate.

Accuracy was assessed by analyzing a series of spiked samples. The

recovery tests were carried out on 4 different types of wine to which standard solutions were added at concentrations ranging from 0.02 $\mu\text{g/mL}$ to 400 $\mu\text{g/mL}$ in order to match the natural concentrations. The addition of the standards caused a 10% dilution of the matrix (v/v). These samples were then analyzed like all the other samples. Recoveries were satisfactory and ranged from 85% for Cr to 109% for Sr. The determination of Ba had been also performed, but an unacceptable recovery was obtained for this metal, so it was not considered in the present study.

2.3. Data analysis

Systat software for Windows Version 13 (Systat Software Inc., USA) was used for statistical analysis and to produce graphs. Principal Component Analysis (Jackson, 2004) was applied as a multivariate technique for exploratory data analysis. Shapiro-Wilk test was used for checking normality. The two groups of samples (conventional and organic) were compared by two-sample t-test (for Al, As, B, Ca, Co, K, Mg, Mn, Na, Pb, and Zn) and by Mann-Whitney test (for Cd, Cr, Cu, Fe, Li, Ni, Sr, and V), as non-parametric analog of the two-sample t-test. A p-value <0.05 was considered to indicate a significant difference between conventional and organic wines.

3. Results and discussion

A summary of the results obtained is shown in Table 1. For each element, the atomic/ionic line, the wavelength (nm) used for the determination and the detection limit of the method (DL) are also reported. DL, expressed in $\mu\text{g/mL}$, is the average of 3 results obtained on different days, considering the instrumental detection limit (computed as 3 times the standard deviation of blank) and the sample dilution factor.

Principal component analysis (PCA) was used in order to assess if any anomalous sample was present in the dataset (Wold et al., 1987). Since no outlier was detected, all data were considered in the following discussion. Moreover PCA showed no separation between organic and conventional wines. The results of PCA are shown in Fig. 1. Statistical tests (two-sample t-test and Mann-Whitney test) were applied to verify if the wine treatment has a significant effect on the mineral content. Among the 19 elements analyzed, only Ni, with a p-value of 0.015, showed a higher concentration in organic wines (mean 0.027 $\mu\text{g/mL}$) with respect to conventional wines (mean 0.012 $\mu\text{g/mL}$). This is shown in Fig. 2, where the distributions of the measured concentrations are reported as box-and-whiskers plot (Krzywinski and Altman, 2014) for the two

Table 1

Mean ($\pm$ standard deviation) and median concentrations (as $\mu\text{g/mL}$) of the elements determined in samples of organic ($n = 11$) and conventional ($n = 12$) white wines from Italy are reported together with the atomic/ionic line, the wavelength (nm) and the detection limit (DL, $\mu\text{g/mL}$).

Element atomic/ionic	Wavelength (nm)	DL ($\mu\text{g/mL}$)	Mean ($\mu\text{g/mL}$) $\pm$ SD		Median ($\mu\text{g/mL}$)	
			Organic	Conventional	Organic	Conventional
Al I	394.401	0.04	0.402 $\pm$ 0.237	0.509 $\pm$ 0.316	0.386	0.499
As I	189.042	0.01	0.092 $\pm$ 0.024	0.092 $\pm$ 0.024	0.094	0.094
B I	249.773	0.09	4.346 $\pm$ 1.446	4.109 $\pm$ 1.324	4.214	3.914
Ca II	396.847	2.3	72.1 $\pm$ 22.6	76.2 $\pm$ 17.9	70.0	76.1
Cd I	228.802	0.001	0.003 $\pm$ 0.001	0.003 $\pm$ 0.001	0.003	0.003
Co II	228.616	0.002	0.005 $\pm$ 0.001	0.005 $\pm$ 0.001	0.005	0.004
Cr II	284.325	0.007	0.025 $\pm$ 0.016	0.021 $\pm$ 0.009	0.024	0.020
Cu I	324.754	0.002	0.088 $\pm$ 0.145	0.076 $\pm$ 0.084	0.043	0.045
Fe II	259.940	0.08	0.703 $\pm$ 0.314	0.842 $\pm$ 0.876	0.757	0.447
K I	766.490	24	780.0 $\pm$ 183.0	674.1 $\pm$ 166.4	808.7	682.8
Li I	670.784	0.001	0.009 $\pm$ 0.009	0.009 $\pm$ 0.008	0.008	0.007
Mg II	279.533	2.4	81.9 $\pm$ 10.1	83.6 $\pm$ 14.7	84.4	82.6
Mn II	257.610	0.06	0.685 $\pm$ 0.256	0.706 $\pm$ 0.206	0.694	0.742
Na I	589.592	0.60	21.1 $\pm$ 9.3	16.9 $\pm$ 9.6	19.3	14.1
Ni II	231.604	0.002	0.027 $\pm$ 0.020	0.012 $\pm$ 0.005	0.021	0.011
Pb II	220.353	0.01	0.017 $\pm$ 0.008	0.020 $\pm$ 0.006	0.018	0.020
Sr II	421.552	0.08	0.565 $\pm$ 0.406	0.633 $\pm$ 0.619	0.462	0.429
V II	290.882	0.003	0.020 $\pm$ 0.027	0.017 $\pm$ 0.020	0.009	0.009
Zn I	213.856	0.008	0.474 $\pm$ 0.195	0.514 $\pm$ 0.245	0.448	0.468

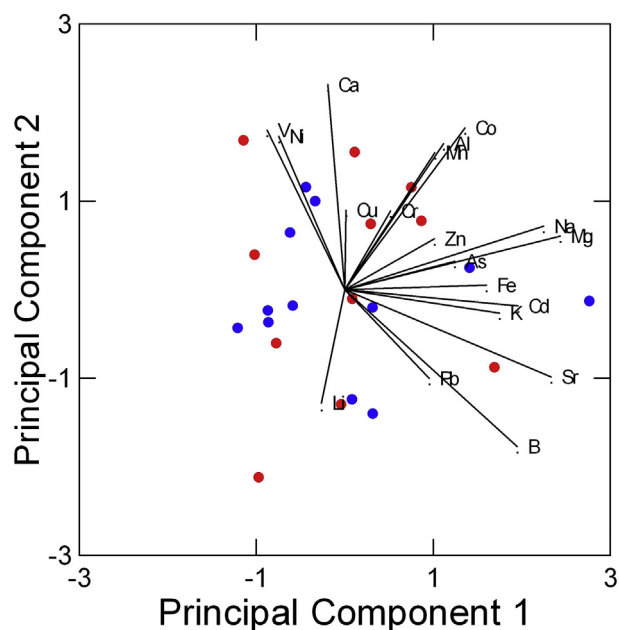


Fig. 1. Results of Principal Component Analysis applied to the data of 23 white wines described by the concentrations of 19 trace elements (blue = conventional; red = organic).

categories considered.

Examining literature data, no agreement was found among the results obtained in the different studies on organic and conventional wines. Dutra et al. (2018) analyzed Fe, Mn and Cu in a limited number of red wine samples ($n = 3$) and they concluded that it was “not possible to affirm that there are considerable differences between organic and conventional products”. Čepo et al. (2018) analyzed 15 elements, including Ni, in 16 red and 10 white wines and the only differences found were that Mg and Pb showed lower concentrations in organic wines. Vrček et al. (2011) analyzed 24 elements, including Ni, in 6 samples of white wine

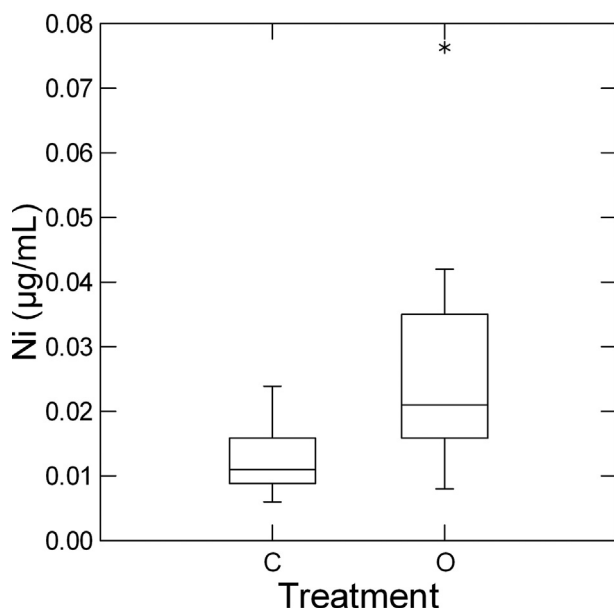


Fig. 2. Box-and-whiskers plots of the concentrations ($\mu\text{g/mL}$) of Ni in conventional (C) and organic (O) white wines from Italy. In each box the central line marks the median of the data; the edges are at the first and third quartiles; the whiskers show the range of values falling within the interquartile range multiplied by 1.5; values falling outside that interval are plotted with asterisks.

and 4 of red wine. They observed that Al, V, Co, Ni and Ga concentrations increased from organic to conventional wines, while Cr, Zn, Se, Mo, Cd, In, Sn, Tl and Pb did not show specific trends. For Cu, Fe, Mn and As differences are not clear, since organic samples showed higher or lower concentrations depending on the wine variety. An interesting number of samples ($n = 27$) of white wine were analyzed for the concentration of 14 elements by Koreňová and Suhaj (2012): significant differences were found only for Cu and Fe, showing lower concentrations in organic wines with respect to conventional ones. In their study, Ni was not included among the elements taken into consideration.

Actually in a variety of foodstuffs other than wine (González et al., 2019) no significant difference in trace element content was found between conventional and organic products.

4. Conclusions

There are not many works reporting comparisons between the content of trace metals in samples of wine obtained from traditional and organic methods. Furthermore, the number of samples analyzed is frequently very low and the comparisons have a limited statistical meaning. Since there is no agreement between the differences reported in the works examined, it can be concluded that the different processes used in wine production do not lead to significant differences in trace element content.

Declarations

Author contribution statement

Giuliana Drava & Vincenzo Minganti: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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References

- Cabrita, M.J., Martins, N., Barrulas, P., Garcia, R., Dias, C.B., Pérez-Álvarez, E.P., Costa Freitas, A.M., Garde-Cerdán, T., 2018. Multi-element composition of red, white and palhete amphora wines from Alentejo by ICPMS. *Food Control* 92, 80–85.
- Čepo, D.V., Pelajić, M., Vrček, I.V., Krivohlavek, A., Zuntar, I., Karoglan, M., 2018. Differences in the levels of pesticides, metals, sulphites and ochratoxin A between organically and conventionally produced wines. *Food Chem.* 246, 394–403.
- Dutra, M.D.P., Rodrigues, L.L., de Oliveira, D., Pereira, G.E., Lima, M.D., 2018. Integrated analyses of phenolic compounds and minerals of Brazilian organic and conventional grape juices and wines: validation of a method for determination of Cu, Fe and Mn. *Food Chem.* 269, 157–165.
- EC, 2018. EU Agricultural Outlook for Markets and Income, 2018–2030. European Commission, DG Agriculture and Rural Development, Brussels. Available from: <https://ec.europa.eu/agriculture/>

- ://ec.europa.eu/info/sites/info/files/food-farming-fisheries/farming/documents/meat-term-outlook-2018-report_en.pdf. (Accessed 5 September 2019).
- EC, 2019. European Commission - Directorate-General for Agriculture and Rural Development. EU Wine Market Data Portal. Available from: https://ec.europa.eu/agriculture/wine/statistics_en. (Accessed 5 September 2019).
- EU, 2012. COMMISSION IMPLEMENTING REGULATION (EU) No 203/2012 of 8 March 2012 Amending Regulation (EC) No 889/2008 Laying Down Detailed Rules for the Implementation of Council Regulation (EC) No 834/2007, as Regards Detailed Rules on Organic Wine. Available from: <https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:071:0042:0047:EN:PDF>. (Accessed 5 September 2019).
- Garaguso, I., Nardini, M., 2015. Polyphenols content, phenolics profile and antioxidant activity of organic red wines produced without sulfur dioxide/sulfites addition in comparison to conventional red wines. *Food Chem.* 179, 336–342.
- González, N., Marqués, M., Nadal, M., Domingo, J.L., 2019. Occurrence of environmental pollutants in foodstuffs: a review of organic vs. conventional food. *Food Chem. Toxicol.* 125, 370–375.
- Ibanez, J.G., Carreon-Alvarez, A., Barcena-Soto, M., Casillas, N., 2008. Metals in alcoholic beverages: a review of sources, effects, concentrations, removal, speciation, and analysis. *J. Food Compos. Anal.* 21, 672–683.
- Jackson, J.E., 2004. A User's Guide to Principal Components. John Wiley & Sons, Inc.
- Koreňovská, M., Suhaj, M., 2012. Chemometric prediction of wines affiliation with organic and conventional production systems through their elemental profiles. *J. Food Nutr. Res.* 51, 23–32. Available from: <http://www.vup.sk/en/index.php?mainID=1&navID=34&version=2&volume=51&article=1836>. (Accessed 5 September 2019).
- Krzywinski, M., Altman, N., 2014. Visualizing samples with box plots. *Nat. Methods* 11, 119–120.
- Mirabal-Gallardo, Y., Caroca-Herrera, M.A., Muñoz, L., Meneses, M., Laurie, V.F., 2018. Multi-element analysis and differentiation of Chilean wines using mineral composition and multivariate statistics. *Cienc. Investig. Agrar.* 45, 181–191.
- Mulero, J., Pardo, F., Zafrilla, P., 2009. Effect of principal polyphenolic components in relation to antioxidant activity in conventional and organic red wines during storage. *Eur. Food Res. Technol.* 229, 807–812.
- Mulero, J., Pardo, F., Zafrilla, P., 2010. Antioxidant activity and phenolic composition of organic and conventional grapes and wines. *J. Food Compos. Anal.* 23, 569–574.
- OIV, 2018. Statistical Report on World Vitiviniculture. International Organisation of Vine and Wine. Available from: <http://www.oiv.int/public/medias/6371/oiv-statistical-report-on-world-vitiviniculture-2018.pdf>. (Accessed 5 September 2019).
- Patrignani, F., Montanari, C., Serrazanetti, D.I., Braschi, G., Vernocchi, P., Tabanelli, G., Parpinello, G.P., Versari, A., Gardini, F., Lanciotti, R., 2017. Characterisation of yeast microbiota, chemical and sensory properties of organic and biodynamic Sangiovese red wines. *Ann. Microbiol.* 67, 99–109.
- Pérez-Álvarez, E.P., García, R., Barrulas, P., Dias, C., Cabrita, M.J., Garde-Cerdán, T., 2019. Classification of wines according to several factors by ICP-MS multi-element analysis. *Food Chem.* 270, 273–280.
- Pohl, P., 2007. What do metals tell us about wine? *Trends Anal. Chem.* 26, 941–949.
- Tariba, B., 2011. Metals in wine-impact on wine quality and health outcomes. *Biol. Trace Elem. Res.* 144, 143–156.
- Tassoni, A., Tango, N., Ferri, M., 2013. Comparison of biogenic amine and polyphenol profiles of grape berries and wines obtained following conventional, organic and biodynamic agricultural and oenological practices. *Food Chem.* 139, 405–413.
- Thiel, G., Geisler, G., Blechschmidt, L., Danzer, K., 2004. Determination of trace elements in wines and classification according to their provenance. *Anal. Bioanal. Chem.* 378, 1630–1636.
- Tobolková, B., Polovka, M., Belajová, E., Koreňovská, M., Suhaj, M., 2014. Possibilities of organic and conventional wines differentiation on the basis of multivariate analysis of their characteristics (EPR, UV-Vis, HPLC and AAS study). *Eur. Food Res. Technol.* 239, 441–451.
- Vázquez, E.S., Segade, S.R., Gomez, E.F., 2013. Incidence of the winemaking technique on metal content and phenolic composition of red wines. *Int. J. Food Prop.* 16, 622–633.
- Volpe, M.G., La Cara, F., Volpe, F., De Mattia, A., Serino, V., Petitto, F., Zavalloni, C., Limone, F., Pellicchia, R., De Prisco, P.P., Di Stasio, M., 2009. Heavy metal uptake in the enological food chain. *Food Chem.* 117, 553–560.
- Vrček, I.V., Bojić, M., Žuntar, I., Mendaš, G., Medić-Šarić, M., 2011. Phenol content, antioxidant activity and metal composition of Croatian wines deriving from organically and conventionally grown grapes. *Food Chem.* 124, 354–361.
- Wold, S., Esbensen, K., Geladi, P., 1987. Principal component analysis. *Chemometr. Intell. Lab. Syst.* 2, 37–52.