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Research Article

Production Method and Wine Style Influence Metal Profiles in Sparkling Wines

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Abbreviations Used: Ag, Silver; Al, Aluminum; As, Arsenic; B, Boron; Ba, Barium; Be, Beryllium; Ca, Calcium; Cd, Cadmium; Co, Cobalt; Cr, Chromium; Cu, Copper; Fe, Iron; K, Potassium; Mg, Magnesium; Mn, Manganese; Mo, Molybdenum; Na, Sodium; Ni, Nickel; Pb, Lead; Sb, Antimony; Se, Selenium; Sn, Tin; Sr, Strontium; Ti, Titanium; Tl, Thallium; U, Uranium; V, Vanadium; Zn, Zinc.

Abstract: The elemental composition of wine provides information important to origin, authenticity, and sensory considerations. While various wine regions and varieties of still wines have been extensively studied, limited research has evaluated the metal profile of sparkling wines, which may be present in the bottle-fermented Traditional method (TM) or tank-fermented Charmat method (CM), in rosé or non-rosé styles. In this study, 73 commercial sparkling wines from Canada’s Niagara Peninsula were analyzed by inductively coupled plasma–optical emission spectrometry (ICP-OES) and inductively coupled plasma–mass spectrometry (ICP-MS) to quantify 28 metal ions (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, U, V, Zn). All metal levels were below internationally regulated maximum limits. Higher mean levels of Cr, Ni, and Sr (0.021 ± 0.008 mg/L, 0.018 ± 0.004 mg/L and 0.32 ± 0.07 mg/L, respectively) and lower mean levels of B (3.0 ± 0.6 mg/L) were identified in CM compared to TM wines. Cr and Ni are of particular interest due to their association with stainless-steel contact during CM production. Additionally, results identified higher mean levels of K (613 ± 153 mg/L) and lower mean levels of Cu (0.034 ± 0.036 mg/L) in rosé compared with non-rosé style wines. These results represent the first investigation of metal content in Canadian sparkling wines and identify important elemental differences related to production technique which can inform future authenticity assessments.

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Key words: elemental composition; multi-elemental analysis; Niagara Peninsula; sparkling wine; trace elements

Introduction

The elemental composition of wine is the consequence of both natural sources and human intervention, and provides important information related to origin, authenticity, toxicological, sensory and nutritional considerations (Tariba 2011, Viviers et al. 2013, Gajek et al. 2021). Specific trace elements are of special interest due to their impact on consumer health such as arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb), which are toxic at high concentrations (Bora et al. 2018, Dumitriu et al. 2019, Fabjanowicz and Plotka-Wasylka 2021). In order to control wine metal levels and ensure consumer safety, regional and international regulatory bodies including the International Organisation of Vine and Wine (OIV) have established maximum acceptable limits for several metal species (Supplementary Materials Table S1) (International Organisation of Vine and Wine 2015).

Multiple factors including soil type, geography, water resources, climate, grape variety, grape maturity, agricultural practices (e.g., foliar sprays, herbicides, fungicides), environmental pollution, and winemaking strategies (e.g., additives, equipment, fining agents) contribute to the type and concentration of metal ions in juice and wine (Tariba 2011, Fabjanowicz and Plotka-Wasylka 2021, Gajek et al. 2021). Extensive research on still wines have demonstrated the application of trace metal profiles and stable isotope ratios to regionally fingerprint wines for the purposes of tracing quality and authenticating geographic origin (Marisa et al. 2003, Coetzee and Vanhaecke 2005, Rodrigues et al. 2011, Bora et al. 2018, Rodrigues et al. 2020, Gajek et al. 2021). In addition to metal levels derived from the growing

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site, anthropogenic inputs during winemaking can introduce or modify individual metal levels, thereby altering the metal composition while processing of grapes from juice to wine. Total metal levels generally decrease during fermentation and ageing due to their precipitation, or co-precipitation with suspended solids (Marisa et al. 2003). Further, wine quality parameters are closely linked to metal ion levels, which can influence yeast nutrition during fermentation, redox processes, haze formation, color stability, acidity, and off-flavor development (Esparza et al. 2005, Tariba 2011, Viviers et al. 2013, Morozova et al. 2014). For example, increased levels of copper (Cu), aluminum (Al), iron (Fe), nickel (Ni), and zinc (Zn) can form tannin and protein haze complexes (Esparza et al. 2005), generating undesirable sensory and color changes in the wine. Additionally, high levels of Cu(II) and Fe(III) ions in wine (above 1 and 7 mg/L, respectively) can impart bitter and metallic tastes (Tariba 2011, Morozova et al. 2014).

While the metal composition of red and white still wines has been extensively investigated within winemaking regions and across different grape varieties, sparkling wine remains relatively under-examined. Sparkling wine is an expanding market which accounts for approximately 7% of global wine production (International Organisation of Vine and Wine 2020). In Canada's province of Ontario, the Niagara Peninsula is the country's largest viticultural area, containing two regional appellations and 10 sub-appellations regulated and administered by the Vintners Quality Alliance of Ontario (VQAO). Ontario sparkling wine production is increasing, as shown by a 140% increase in production volume between the 2014 – 2019 harvests, resulting in nearly 1.5 million L of sparkling wine produced in 2019 (Vintners Quality Alliance Ontario 2015, 2020). Therefore, understanding the contribution of sparkling wine metal composition to wine quality, as well as its application to authenticity verification are increasingly relevant.

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Sparkling wine production involves unique processing steps which can influence metal composition. Initially, a primary fermentation transforms the juice into a still base wine, which subsequently undergoes a secondary fermentation. Conditions for the second fermentation delineate the two primary methods of sparkling wine production, which represent the largest categories of international sparkling wine: second fermentation in the same bottle that is later purchased by the consumer (Traditional method, TM), or second fermentation in an isobaric stainless-steel tank (Charmat method, CM) (Figure 1). During each elaboration process, yeast, sugar, and nutrients are added to the vessel to initiate the second fermentation, thereby producing carbon dioxide (CO_2), and contributing effervescence to the wine. TM wines typically have minimum legal ageing requirements on lees, or *sur lies*, (average *sur lies* ageing duration of 12 months), although this length varies with region and vintage or non-vintage declarations. In Ontario, TM sparkling wines with a vintage declaration require a legal minimum of 12 months ageing *sur lies* while non-vintage TM wines may be aged for only nine months, according to the Government of Ontario website (https://www.ontario.ca/laws/regulation/000406). Common TM wines include Champagne (France), Crémant d'Alsace (France and Luxembourg), and Cava (Spain). CM sparkling wines such as Prosecco (Italy) and Sekt (Germany and Austria) are generally available at a lower price than TM wines due to the comparatively short secondary fermentation process (1-6 weeks) and less-intensive production regime. Additionally, rosé or white (non-rosé) sparkling wine styles can be produced by either TM or CM techniques. During rosé production, red-skinned grapes are pressed, and their juice subsequently remains in contact with grape solids for a short duration (several hours) to extract the desired hue and sensory attributes. Alternatively, white sparkling wines are produced by immediately separating juice from grape solids post-pressing. Rosé style wines are likely to contain elevated metal content compared to white sparkling wines due to

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the maceration process, which extracts metals localized in grape skin and seed structures (Pérez Cid et al. 2019).

Several research groups have investigated the application of metal fingerprinting and isotopic characterization of Canadian still wines to discriminate between wine growing regions (Greenough et al. 1997, Taylor et al. 2003, Greenough et al. 2005, Vinciguerra et al. 2016). However, research related to metal content in sparkling wines remains limited. For example, the mineral profile of Spanish Cava, a TM sparkling wine, was studied for wines produced within a single growing region (Jos et al. 2004). Other authors have examined sparkling wine metal profiles to regionally discriminate sparkling wines by country of origin (Jos et al. 2004, Yamashita et al. 2019, Rodrigues et al. 2020). Available data on the levels of metal species identified in sparkling wines is shown in Table 1. Notably, there is currently no data on sparkling wines produced in North America, including Canada, which is a rapidly expanding cool climate region for sparkling wine production (British Columbia Liquor Distribution Branch 2017, 2021, Vintners Quality Alliance Ontario 2015, 2020). Additionally, to the best of our knowledge, current literature does not compare the elemental composition of TM and CM wines, nor the impact of rosé and non-rosé styles on sparkling wine metal profiles. These research gaps informed the present study.

The primary objective of this analysis was to survey the metal composition of sparkling wines produced in Canada’s Niagara Peninsula and assess differences related to production method (i.e., TM and CM) and style (i.e., rosé, non-rosé). By evaluating wines from a single winegrowing region, a clear understanding of the effects of sparkling winemaking techniques on metal profiles may be assessed.

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2.0 Materials & Methods

2.1 Instrumentation

The analysis of 28 metal ions was carried out by inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–optical emission spectrometry (ICP-OES) techniques. Samples were analyzed by an Agilent ICP-MS 7700x mass spectrometer (Agilent Technologies, Santa Clara, CA) operating in the following modes: no gas and He (KED-Kinetic Energy Discrimination) to remove interferences as required. Ions for ICP-MS analysis are shown in Table 2. Boron (B) was subsequently analyzed by a Thermo Scientific iCAP 7400 ICP-OES Dual-View spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) due to analyte concentrations outside of the linear range for the ICP-MS method (0.1 mg/L). B results were obtained with the ICP-OES instrument operating in axial mode. The wavelength used for elemental detection by ICP-OES was 249.678 nm for B. Standard chemical analysis of wine samples was not carried out as the scope of this study was focused solely on comparing metal composition rather than wine chemical parameters.

2.2 Sparkling Wine Samples

A total of 73 sparkling wines produced in Canada’s Niagara Peninsula were analyzed. Samples were extracted from commercial wine products acquired at liquor retailers or directly from various wineries. Upon collection, all bottles were immediately transported to the Cool Climate Oenology and Viticulture Institute (CCOVI) at Brock University and stored horizontally for approximately 2 months in the wine cellar at 14°C prior to analysis. All wines used in this study were sampled from 750 mL glass bottle formats. Sparkling wines included Traditional method (TM; 43 non-rosé and 11 rosé) and Charmat method (CM; 15 non-rosé and four rosé) wines. The higher proportion of TM and non-rosé wines

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approximately reflects the local industry's emerging production trends towards dry style sparkling wines (Vintners Quality Alliance Ontario 2021). Samples were an amalgamation of single grape variety wines and blends of several varieties. All wines for analysis were certified by the Vintners Quality Alliance Ontario (VQAO), a regulatory body within the province intended to preserve wine quality standards and authenticity of origin. Information pertaining to geographical origin was collected from VQA label information and directly from producers. Vintage and closure types (cork or crown cap) for individual wines can be found in Supplementary Materials (Table S2).

2.3 Reagents

All solutions were prepared from ultra-pure reagents. Ultrapure deionized water with ≥ 18.0 MΩ·cm resistivity was obtained from a Barnstead™ E-Pure™ water purification system (Thermo Fisher Scientific, Waltham, MA). Concentrated trace metal grade nitric acid (HNO_3, 67-70% v/v) and concentrated hydrochloric acid (HCl, 37% v/v) were purchased from VWR (Aristar® Plus, VWR International, Radnor, PA). An ionization suppressant of 0.4% w/v cesium chloride (CsCl, 99.9% v/v) was utilized as an internal standard for ICP-OES via online addition and was purchased from Sigma-Aldrich (ReagentPlus®, St. Louis, MO).

Multi-element ICP-MS calibration standards of Standard 1, Standard 2A, Standard 3 and Standard 4 were purchased from Agilent (Santa Clara, CA, USA) at 10 mg/L stock concentrations. Five calibration solutions were prepared to a maximum of 0.1 mg/L for Standard 2A and 0.01 mg/L for Standards 1, 3 and 4 as defined in Supplementary Materials (Table S3). For major ions (Al, Ca, Fe, K, Mg, Na), additional single-element 10000 mg/L stock solutions acquired from SCP Science (Baie D'Urfé, Canada) and Inorganic Ventures (Christiansburg, VA) were employed to extend the calibration

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range beyond 0.1 mg/L. Additional 50 mg/L standards were used to extend the linear range for Al, Ca, Fe, K, Mg, and Na. A further 200 mg/L standard was added to extend the linear range for K.

Certified EnviroMAT™ EU-H matrix reference standard for elemental analysis of wastewater (high levels) was purchased from SCP Science (Baie D'Urfé, Canada) and prepared at a 1:500 dilution (ICP-MS) and 1:50 dilution (ICP-OES). Online internal standards of Sc, In, and Bi were used for ICP-MS; Sc and Y internal standards were employed for ICP-OES (SCP Science, Baie D'Urfé, Canada). Ultrapure grade plasma gas (Ar, argon, 99.999% purity) and collision gas (He, helium, grade 5.0) were purchased from MEGS (Pointe-Claire, Canada) and Messer (Mississauga, Canada), respectively.

2.4 Sample Treatment and Analysis

Sample preparation and analysis was conducted at the Queen’s University Analytical Services Unit following procedures based on the U.S. Environmental Protection Agency (USEPA) Method 200.8 for determination of trace elements in waters by ICP-MS (USEPA 1994). B analysis by ICP-OES was carried out as per the USEPA Method 6010D for trace elements in aqueous solutions (USEPA 2018).

Wines were sampled directly from freshly opened bottles, transferred to 15 mL sterile conical tubes (VWR, Radnor, PA) and stored at 4°C for 2-3 weeks until analysis. Single bottles of each wine were evaluated, consistent with previous studies that have surveyed metal composition of wines (Cabrera-Vique et al. 1997, Teissedre et al. 1998, Jos et al. 2004, Paustenbach et al. 2016, Gajek et al. 2021). All wine samples were analyzed in duplicate. Samples were degassed and diluted 10-fold by diluting 2.5 mL wine to 25 mL with ultrapure deionized water. Samples (25 mL, as prepared) and quality control (QC) solutions (blanks, duplicates, reference solutions) were measured into DigiTubes (SCP Science, Baie D'Urfé, Canada) with 0.25 mL concentrated trace grade HNO_3 and 0.125 mL concentrated HCl for digestion at 90°C for 240 minutes. Dilution and digestion aims to reduce matrix

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effects associated with organic and inorganic compounds in the wine (Moehring and Harrington 2021). Samples were cooled and diluted to 25 mL with double deionized water and analyzed by ICP-MS and/or ICP-OES. Method preparation including digestion was carried out for all method blanks, duplicates, and certified reference standards to minimize matrix effects.

2.5 Quality Assurance

Online internal standards of Sc, In and Bi were used with ICP-MS whereas Sc and Y were utilized for ICP-OES analysis. In addition, 0.4% w/v CsCl was added as an ionization suppressant for the OES system by means of a third channel in the peri-pump. Quality assurance solutions of one method blank, one matrix reference solution and two control duplicates were included for every 12 samples analyzed. Sample replicates showed a mean relative standard deviation of 3.3 ± 5.6%. Certified reference material (EU-H) showed a mean percent recovery of 95.4 ± 3.9% ($n = 9$) compared to certified values. All blanks showed metal concentrations below detection limits for both ICP-MS and ICP-OES.

2.6 Statistical Analysis

XLSTAT Version 2021.1.1 (Addinsoft, NY, USA) software was used for statistical analysis in Microsoft® Excel® for Mac (Version 16.47.1, 2021, Microsoft®). Reported values represent the final concentrations of metal ions in wine without dilution. The accepted level of significance for all statistical tests was established at $p = 0.05$.

For evaluating the variability of individual metal levels by production method or style, multiple analysis of variance (MANOVA) was carried out for elements detected in all wine samples (B, Ca, Mg, Mn, K, Na, Sr, Zn). A Shapiro-Wilks test was run to verify the normality of residuals followed by a one-way analysis of variance (ANOVA) with Tukey’s post-hoc means separation tests. Censored data where

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elements showed below limit of detection (LOD) values were excluded from this portion of the analysis. Due to the high proportion of non-detected (<LOD) values for many metal ions, this strategy of removing <LOD values from summary statistics therefore avoids treating <LOD values as observed measurements. While substitution techniques (e.g., substituting <LOD values for 0, LOD, or LOD/2) have been previously used in environmental research, they are widely considered to be an outdated and inappropriate method for handling censored data due to their effect on skewing statistics when high levels of non-detected values are present (Wood et al. 2011, Shoari and Dubé 2018). Differences in the proportion of censored data as well as unique LOD thresholds for each metal informed our decision to remove <LOD values from this portion of the analysis to visualize the range of detected values found in sparkling wines. Censored and non-normally distributed elemental datasets were analyzed by Kruskal-Wallis non-parametric tests to determine differences in mean rank due to production method and style. To assist with interpreting summary results, *n* values are reported for all analyses where <LOD values were eliminated from interpretation (Table 3, Figures 2 & 3).

To further evaluate relationships between metal ions and sparkling wine production techniques, Spearman's rank correlation matrix was used to identify relationships between metals that were present in all wine samples (B, Ca, Mg, Mn, K, Na, Sr, Zn), due to the non-normal distribution of several metals in this analysis (Mg, Mn, Na, Sr, Zn). Principal component analysis (PCA) was used to explore relationships between metal composition and production method or wine style.

3.0 Results

The mineral composition of 73 commercial sparkling wines produced in Canada's Niagara Peninsula were analyzed. Of the 28 quantified metal ions (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg,

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Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Ti, Tl, U, V, Zn), silver (Ag) and titanium (Ti) were not detected in any samples and were therefore removed from our results. Identified metal levels followed internationally recommended maximum limits for wine established by the OIV. Metal concentrations with >LOD values are reported in Table 3 by production method in addition to the overall detected range. Individual sample results are available in Supplementary Materials (Table S4) as well as box and whisker plots for each element to visualize the distribution of data for both production method and style (Figures S1-S27).

Significant differences between sparkling wine production methods were identified. Trends toward higher mean levels of B, Cr, Ni and strontium (Sr) levels were detected in CM wines compared to TM wines at the 95% confidence interval, as shown in Figure 2. B was present in all wine samples (CM = 19 wines, TM = 54 wines) and normally distributed (Shapiro-Wilks test) and was therefore evaluated by one-way ANOVA. Sr was also present in all wine samples, although non-normally distributed (Shapiro-Wilks test) and was subsequently assessed by a Kruskal-Wallis test. Cr was <LOD in five CM wines (26%) and 19 TM wines (35%), and Ni was <LOD in three CM wines (16%) and 11 TM wines (20%). All samples with <LOD values were analyzed by Kruskal-Wallis tests, and non-detected values were eliminated from this assessment. When comparing rosé and non-rosé style sparkling wines (Figure 3), trends toward higher mean levels of K were identified in rosé wines, as well as increased Cu in non-rosé wines. K was present in all wine samples (non- rosé = 58 wines, rosé = 15 wines) and normally distributed (Shapiro-Wilks test), and thus analyzed by a one-way ANOVA. However, Cu was <LOD in 8 non-rosé wines (14%) and 5 rosé wines (33%).

The Spearman correlation matrix for metals found in all wines, namely B, Ca, Mg, Mn, K, Na, Sr, Zn, is shown in Table 4. Low correlation ($\rho < 0.4$) relationships were shown to exist between B and

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K ($\rho = 0.267$; $p < 0.05$), Ca and Mn ($\rho = 0276$; $p < 0.05$), Mg and Mn ($\rho = 0.318$; $p < 0.01$), Mg and Na ($\rho = -0.250$; $p < 0.05$), Mg and Sr ($\rho = 0.372$; $p < 0.01$), Mn and K ($\rho = 0.293$; $p < 0.05$), and Mn and Zn ($\rho = 0.384$; $p < 0.001$). In subsequent analyses, wines were separated by production technique for Spearman analysis to identify process-based relationships for metal ions. Table S5 shows that for TM wines ($n = 54$), many of the correlations in the overall dataset remain consistent. The Spearman correlation matrix for CM wines ($n = 19$) is shown in Table S6, where moderate correlations ($0.4 > \rho < 0.7$) exist between B and Na ($\rho = 0.518$; $p < 0.05$), Ca and K ($r = 0.482$; $p < 0.05$), along with Mg and Sr ($\rho = 0.474$; $p < 0.05$). The Spearman matrix for non-rosé sparkling wines ($n = 58$) is presented in Table S7 where only weak correlations between metals were observed, including B and K ($\rho = 0.2743$; $p < 0.05$); B and Sr ($\rho = -0.282$; $p < 0.05$); Mg and Mn ($\rho = 0.322$; $p < 0.05$); Mg and Sr ($\rho = 0.315$; $p < 0.05$); and Mn and Zn ($\rho = 0.369$; $p < 0.01$). For rosé sparkling wines ($n = 15$) shown in Table S8, moderate correlations were identified between Ca and Mn ($\rho = 0.682$; $p < 0.05$); Ca and K ($\rho = 0.541$; $p < 0.05$); Mg and Sr ($\rho = 0.659$; $p < 0.01$); Mn and K ($\rho = 0.559$; $p < 0.05$); Mn and Zn ($\rho = 0.644$; $p < 0.05$); and Sr and Zn ($\rho = 0.554$; $p < 0.05$).

PCA of the reduced dataset was carried out for sparkling wines ($n = 73$), with the first three principal components accounting for approximately 60% of the variability. The biplot for principal component 1 (PC1) and principal component 2 (PC2) presented in Figure 4 shows that PC1 explains approximately 24% of the total variance while PC2 accounts for 19%. Wines are also identified by production method (Figure 4a) and style (Figure 4b). Mn was the only element with a strong positive factor loading (>0.75), where it contributed to the PC1 component. Factor loadings for Mg and Zn are moderate positive contributors (0.5-0.75) to PC1, while B, K and Sr provide moderate positive contributions to PC2. Few

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elements were located on the negative component of PC1, apart from minor contributions by B and Na. In the positive quadrant of PC1 and PC2, the strong positive relationship between Zn and Mn is supported by a weak Spearman correlation ($\rho = 0.384$; $p < 0.001$), and in the positive quadrant of PC1 and the negative quadrant of PC2, Ca and Sr appear to be highly associated, although their Spearman correlation value of 0.141 is not significant. Our PCA results indicate that no clear separation is evident between sparkling wines when identified according to production technique (Traditional method vs. Charmat method) or style (rosé vs. non-rosé).

4.0 Discussion

Overall, the metal levels detected in our samples were comparable to those reported in sparkling wine literature (Table 1). It is of note that our maximum concentrations of Al, As, Fe, Mn, and Zn exceeded previously reported maximum levels. However, only single wines in our analysis showed higher mean levels of Al, Fe and Mn. For As, concentrations were approximately 3-fold higher than reported literature values in 48% of our Niagara sparkling wines. Comparatively, mean Zn concentrations were higher than literature values in 52% of our evaluated wines, with the maximum levels approximately 4-fold higher than previously reported. Conversely, for Cd, maximum concentrations in our Niagara sparkling wines were approximately 30-fold lower than previously reported maximum concentrations identified in sparkling wine literature. Cd content is primarily related to fertilizer use, where prolonged or intensive application of high Cd fertilizer leads to substantial accumulation of Cd in the soil, and is subsequently a challenge to remediate (Reilly 1980b). As such, this may indicate that the comparatively young Niagara Peninsula viticultural area has lower Cd accumulation than France and Spain, where considerably higher Cd levels were reported in sparkling

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wine (Jos et al. 2004). Further assessment is necessary to validate this hypothesis. Additionally, elevated levels of heavy metals including Cd, As, and Pb have been linked to the use of diatomaceous earth (DE) as a filtration aid during wine and beer production (Redan et al. 2019). Our reported Fe, K, and Na levels for Niagara wines appear more similar to sparkling wines produced in the Southern hemisphere (i.e., Brazil, Argentina) compared to those of European origin (i.e., France, Spain) (Table 1). The reason for this association is unclear. It is of note that single bottle analysis does not capture bottle variation, particularly in TM sparkling wines where an individual secondary fermentation is carried out per bottle. Although single bottle analyses have been used in previous studies of wine metal composition (Cabrera-Vique et al. 1997, Teissedre et al. 1998, Jos et al. 2004, Paustenbach et al. 2016, Gajek et al. 2021), this source of variation warrants further research.

4.1 PCA

PCA included metals found in all wines, namely B, Ca, Mg, Mn, K, Na, Sr, Zn (Figure 4) with samples identified according to production method (Figure 4a) and style (Figure 4b). Of the metal ions for which significant differences were observed between mean values for production method and style, only B, Sr, and K were included in the PCA due to >LOD values in all wines. Higher mean B levels were identified in TM than CM wines, which is in agreement with the biplot for production method (Figure 4a). The B vector loading in the negative quadrant of PC1 and positive quadrant of PC2 appears strongly associated with many TM wines while no CM wines are strongly associated. Higher mean Sr levels were identified in CM wines compared to TM wines, and the Sr vector loading in the positive quadrant of PC1 and negative quadrant of PC2 appears strongly associated with several CM sparkling wines while few TM wines appear in this region. The PCA biplot of sparkling wine production style (Figure 4b) shows that many rosé wines are isolated to the positive half of PC2, apart from two wines.

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Interestingly, only one rosé wine appears to be negatively related to K content, which agrees with our finding of higher mean K concentrations in rosé compared to non-rosé sparkling wines. Although our wines were collected from a relatively small geographic area of the Niagara Peninsula, elemental composition may also be impacted to varying degrees by vineyard origins and the specific winemaking facility (Hopfer et al. 2015).

4.2 Elemental Composition by Production Method

Differences in certain elemental concentrations were observed between CM and TM products, where higher mean levels of Cr, Ni and Sr were identified in CM wines (0.021 ± 0.008 mg/L, 0.018 ± 0.004 mg/L, and 0.32 ± 0.07 mg/L, respectively) compared to TM wines (0.015 ± 0.004, 0.016 ± 0.011, and 0.24 ± 0.09, respectively). Additionally, higher mean B concentrations were observed in TM wines (3.4 ± 0.8 mg/L) compared to CM wines (3.0 ± 0.6 mg/L). While Cr and Ni may be partially derived from the vineyard soil, they are also used in the production of stainless-steel as an electroplated coating to resist oxidative damage (Reilly 1980c). Cr is extracted into foods and beverages during manufacturing in a pH dependent manner with increased extraction under acidic conditions (Reilly 1980c). Due to the low pH (3.0-3.2) of sparkling wines, the transfer of Cr from stainless-steel to wine during the prolonged tank contact in CM production is reasonable. Further, a study by Cabrera-Vique et al. (1997) demonstrated that Cr content increased with bottle age for various vintages of red wine produced from the same process, vineyard, and winery. The authors suggested that this was due to the extraction of Cr from stainless steel during production as well as chromium oxides leaching from glass pigments in the bottle during ageing. In a study of metal content in still wines from Greece, Cr and Ni had a low positive correlation (Spearman $\rho = 0.421$; $p < 0.05$), which was suggested to be associated with stainless steel fermentation vessels used in production (Skendi et al., 2020). Based on our results, higher mean levels

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of Cr ($p < 0.05$) and Ni ($p < 0.01$) in tank-fermented CM wines could potentially be linked to stainless-steel processing equipment used for the second fermentation and could therefore be useful indicators for authenticating sparkling wine production methods. Further research is required to establish Cr composition in relation to the tank fermented sparkling wine method.

Other identified elements with significant mean differences between production methods, namely B and Sr, are primarily derived from the vineyard environment where they are transported into the plant via the root system during growth. Grapevines (genus *Vitis*) are perennial plants and uptake a significant portion of nutrients between bloom and véraison (berry ripening) when these energy-intensive cycles require nutrients from the soil to be incorporated into the plant (Moyer et al. 2018). B is an essential nutrient for vine growth, however its relationship to higher content with TM production method ($p < 0.05$) remains unclear and may instead be an artifact of the relatively small Niagara Peninsula growing region (est. 17,000 acres of land under vine (Vintners Quality Alliance Ontario 2020)).

Similarly, Sr shows no clear links to production method and requires further investigation as to its higher levels in CM wines. Heavy metals such as Sr have been used to authenticate wines due to their natural occurrence in soil, air, and water sources. In a multi-element analysis of Canadian wines, Sr content was highly discriminating between geographic origin for Canada’s two major wine-producing regions of the Niagara Peninsula and the Okanagan Valley (Taylor et al. 2003). In another study, Sr levels varied significantly between grape varieties (Gajek et al. 2021). While Sr levels may vary during winemaking, the stable $^{87}Sr/^{86}Sr$ isotopic ratio remains unchanged from the vineyard environment through to the finished wine so may be used alone, or in combination with other heavy metal isotopic information for geographical traceability (Bora et al. 2018). Future research into the Sr isotopic ratio of

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CM and TM wines may elucidate possible contaminants in the winemaking process and inform the relationship between finished wine and vineyard soil Sr content.

4.3 Elemental Composition by Wine Style

Rosé style sparkling wines included in our analysis contained higher mean levels of K (613 ± 153 mg/L) compared to non-rosé wines (466 ± 158 mg/L). Maceration in rosé wine production is presumed to be responsible for higher mean K levels in rosé sparkling wines ($p < 0.01$). K is the most abundant element in wine, and is considered a major metal along with Ca, Na, and Mg (Pohl 2007). K is concentrated in grape skins and seeds with a lesser amount localized in the pulp (Pérez Cid et al. 2019), and has been shown to increase in final wines with prolonged maceration during skin contact white wine production (Darias-Martín et al. 2000). In red still wines, K has been identified at higher levels compared to white still wines (Mitić et al. 2014). Therefore, the observed increase of K in rosé sparkling wines is likely due to the maceration of grape skins and seeds with juice prior to fermentation. The origin of K is primarily soil derived, although fertilizers rich in K may also affect these levels (Mpelasoka et al. 2003). The impact of high K levels on organoleptic qualities of wine is principally associated with potassium bitartrate precipitation, leading to decreased tartaric acid and TA (g/L) levels in wine, thereby increasing pH (Ough et al. 1969, Ferreira et al. 1995). The Spearman matrix for rosé style wines (Table S8) indicates that K is moderately correlated with both Ca ($\rho = 0.541$; $p < 0.05$) and Mn ($\rho = 0.559$; $p < 0.05$). Although K is found at several-fold higher concentrations than Ca or Mn, they are all components of grape berries. Thus, maceration in rosé sparkling wine production may also extract Ca and Mn to a lesser extent. It is of note that the cause for higher K levels may also be partly attributed

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to non-production factors including rootstock, grape variety, soil composition, canopy management, and irrigation (Mpelasoka et al. 2003).

Additionally, Cu was significantly higher ($p < 0.05$) in non-rosé sparkling wines (0.080 ± 0.091 mg/L) compared to rosé samples (0.034 ± 0.036 mg/L). However, there is no clear association between Cu levels and winemaking processes for this style. The origins of Cu are primarily associated with various viticultural aspects including environmental pollution, and the use of Cu-based vineyard sprays as pesticides or fungicides (Wilkes 2018). In wine, residual Cu has been implicated in oxidative and reductive spoilage, protein instability and the development of colloidal haze, while also inhibiting microorganisms, thereby impacting wine fermentation (Clark et al. 2015, Claus 2020). During fermentation, Cu is utilized as a yeast micronutrient although its levels decrease substantially post-fermentation when it is reduced to insoluble sulfides and precipitated with flocculating yeast cells (Tariba 2011). However, Cu content may increase as a result of added copper sulfate ($CuSO_4$), which is commonly used as a treatment to remove hydrogen sulfide (H_2S) reductive off-flavors in wine (Pohl 2007, Fabjanowicz and Plotka-Wasylka 2021). The concentration of Cu has also been reported to be higher in grape skins compared to pomace, although this does not explain the higher levels measured in non-rosé style sparkling wines. While the reason for higher Cu levels in non-rosé compared to rosé style sparkling wines remains unclear, it is of note that Cu(II) ions can catalyze the oxidation of polyphenols through reactive oxygen species (ROS) formation, thereby leading to premature browning as well as astringent and metallic tastes (Pohl 2007). The threshold for Cu ions impacting wine sensory characteristics has been reported at 0.5 mg/L (Morozova et al. 2014), and all detected values in Niagara sparkling wines were below this level. Nonetheless, it is important to note that Cu, particularly in tandem with Fe, plays an important role in wine oxidation and browning reactions with direct ties to

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flavor development. According to a study by Morozova et al. (2014), Riesling still wines with 0.5 mg/L Cu and 1 mg/L Fe showed enhanced fruity, fresh, tropical, and citrus aroma qualities under low oxygen (<1.2 mg/L) bottling conditions (Morozova et al. 2014), although these metal levels in elevated oxygen conditions reportedly led to undesirable and oxidized aromas, presumably due to Cu and Fe-catalyzed radical reactions (Morozova et al. 2014). Moreover, wine browning reactions can occur via enzymatic or non-enzymatic pathways, where Cu and Fe are also implicated in initiating these processes (Li et al. 2008). Although enzymatic browning occurs primarily in the grape must during processing, non-enzymatic browning reactions can take place at any stage during the wine's lifetime, including during ageing (Li et al. 2008).

Interestingly, in model systems, various metal ions have been shown to accelerate a specific sub-set of non-enzymatic browning activity called the Maillard reaction, which involves the condensation of amino acids and reducing sugars (Ase et al. 1996, Rizzi 2008, Omari et al. 2021). Maillard reaction-associated compounds have been identified in aged sparkling wine, likely due to the abundance of precursors in this matrix, and contribute desirable roasted and toasted aromatic qualities (Keim et al. 2002, Marchand et al. 2011, Le Menn et al. 2017). There is currently no existing literature on the effects of metal composition on the Maillard reaction in sparkling wine, and as such, the role of metals in the development of desirable aroma compounds during sparkling wine ageing remains poorly understood.

5.0 Conclusion

The results obtained in this study represent the first analysis of metals in sparkling wines produced in North America, and specifically, Canada's Niagara Peninsula. All 73 wines contain metal concentrations within the limits set by the OIV. Moreover, levels were generally in agreement with the

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values previously reported in sparkling wine literature, although our maximum concentrations are higher than those previously reported for As and Zn. Conversely, for Cd, Niagara sparkling wine levels were below previously reported values.

When comparing measured metal ion levels, significant differences were identified for several mean metal levels based on production method and style. Tank-fermented Charmat method wines contained higher mean levels of Cr, Ni and Sr compared to bottle-fermented Traditional method wines, whereas mean B levels were higher in Traditional method wines. Cr and Ni are components of stainless steel and are likely transferred to Charmat method sparkling wines during extended tank contact. Moreover, Cr and Ni content may be useful for differentiating sparkling wines by production method within the Niagara Peninsula and are potential candidates for sparkling wine authenticity markers. Compared to non- rosé sparkling wine styles, higher mean K, as well as lower Cu concentrations were characteristic of rosé wines. While K levels are likely related to the extraction of inorganic components from skins and seeds during maceration, the links to Cu remain unclear.

By reporting the influence of production method and style on the elemental composition of sparkling wine, this study provides context for future investigations on the possible roles of metals during sparkling wine ageing, as catalysts of non-enzymatic Maillard reaction type browning mechanisms and subsequent age-related sparkling wine flavors.

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Table 1. Concentration range (mg/L) of metals previously identified in sparkling wines by country of origin.

Origin	**Concentration (mg/L)**																		Ref
	Al	As	B	Ba	Ca	Cd	Cu	Fe	K	Li	Mg	Mn	Na	Ni	P	Pb	Sr	Zn	
France	0.19–1.21	–	2.12–3.52	0.002–0.31	61.0–105.7	–	0.005–0.021	0.65–1.82	299–567	0.0020–0.0230	51.8–78.9	0.39–0.65	4.0–19.2	–	–	–	0.07–0.46	–	(N. P. Rodrigues et al., 2020; Yamashita et al., 2019) [a]
France	0.56–1.27	0.010–0.017	–	0.025–0.055	65–93	0.0003–0.0018	0.034–0.48	0.8–2.5	265–426	–	72–96	0.6–1	8–18	0.001–0.052	75–170	0.006–0.023	0.22–0.37	0.44–0.74	(Jos, Moreno, González, Repetto, et al., 2004) [b]
Spain	0.6–2.8	0.007–0.016	–	0.031–0.092	59–122	0.0001–0.0190	0.03–0.2	0.5–2.7	338–490	–	58–105	0.4–0.9	11–32	0.001–0.084	50–131	0.001–0.084	0.03–1.06	0.21–0.57	(Jos, Moreno, González, Repetto, et al., 2004) [b]
Spain	0.569–2.782	0.007–0.016	–	0.031–0.092	59.192–122.216	0.0001–0.0191	0.034–0.194	0.516–2.774	338.07–490.16	–	57.984–104.859	0.451–0.940	11.372–32.163	0.001–0.084	50.125–130.681	0.001–0.084	0.031–1.061	0.208–0.575	(Jos, Moreno, González, López-Artíguez, et al., 2004) [b]
Spain	0.40–0.97	–	2.68–4.36	0.02–0.06	90.9–119.6	–	0.005–0.111	0.51–2.00	276–482	0.010–0.023	53.9–92.6	0.48–0.82	6.2–29.1	–	–	–	0.25–1.02	–	(N. P. Rodrigues et al., 2020; Yamashita et al., 2019) [a]
Brazil	0.19–1.46	–	2.04–3.78	0.03–0.13	67.6–140.7	–	0.003–0.230	0.46–4.46	402–1134	0.0018–0.0140	55.2–89.2	1.12–2.86	13.9–83.4	–	–	–	0.15–1.34	–	(N. P. Rodrigues et al., 2020; Yamashita et al., 2019) [c]
Brazil	–	–	–	–	30.2–49.7	–	–	0.36–0.92	332–503	–	42.9–62.6	1.30–1.90	10.0–18.1	–	102–131	–	–	0.62–0.90	(Debastiani et al., 2021)[b]
Argentina	0.18–1.74	–	2.98–14.90	0.001–0.065	34.4–129.0	–	0.003–6.670	0.59–4.46	404–1475	0.014–0.360	56.7–147.5	0.15–1.01	27.6–344.2	–	–	–	0.38–1.29	–	(N. P. Rodrigues et al., 2020; Yamashita

American Journal of Enology and Viticulture (AJEV). doi: 10.5344/ajev.2022.21051

et al., 2019)
[c]

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[a] Only Traditional method, with a diversity of rosé and white grape sources.

[b] Only Traditional method production, in a non-rosé (white) style.

[c] Combination of Traditional and Charmat methods, with a diversity of rosé and white grape sources.

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Table 2. Parameters for ICP-MS analysis of metals in wine, sorted by ion mass.

Element	**Ion (*m/z*)**	**Mode**
Be	9	No Gas
Na	23	He
Mg	24	He
Al	27	No Gas
K[†]	39	He
Ca	44	He
Ti	47	He
V	51	He
Cr	52	He
Mn	55	He
Fe	56	He
Co	59	He
Ni	60	He
Cu	63	He
Zn	66	He
As	75	He
Se	82	No Gas
Sr	88	He
Mo	95	He
Ag	107	He
Cd	111	No Gas
Sn	118	No Gas
Sb	121	He
Ba	137	No Gas
Tl	205	No Gas
Pb	208	No Gas
U	238	No Gas

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Table 3. Metal concentrations detected in Niagara region sparkling wines determined by ICP-MS and ICP-OES with > LOD values for different production methods.

		Overall	Charmat Method (*n* = 19)			Traditional Method (*n* = 54)		
Metal	Reporting Limit (mg/L)	Range (mg/L)	Mean ± SD (mg/L)	Range of quantified values (mg/L)	>LOD in *n* wines	Mean ± SD (mg/L)	Range of quantified values (mg/L)	>LOD in *n* wines
Al	0.05	0.09-5.20	0.69 ± 0.50	0.09-2.00	15	0.82 ± 0.77	0.10-5.20	48
As	0.010	0.011-0.054	0.021 ± 0.013	0.011-0.054	18	0.022 ± 0.009	0.011-0.054	53
B†	0.5	1.7-5.0	3.0 ± 0.6	1.9-4.6	19	3.4 ± 0.8	1.7-5.0	54
Ba	0.010	0.015-0.120	0.042 ± 0.023	0.018-0.120	19	0.035 ± 0.014	0.015-0.082	53
Be	0.0010	0.0010-0.0064	0.0023 ± 0.0018	0.0011-0.0064	10	0.0028 ± 0.0009	0.0010-0.0041	14
Ca	1	36-92	67 ± 13	45-92	19	62 ± 13	36-92	54
Cd	0.00010	0.00010-0.00046	0.00021 ± 0.00013	0.00010-0.00046	11	0.00020 ± 0.00007	0.00011-0.00036	29
Co	0.0050	0.0058-0.0060	0.0058	0.0058	1	0.0060	0.0060	1
Cr	0.010	0.010-0.043	0.021 ± 0.008	0.014-0.043	14	0.015 ± 0.004	0.010-0.028	35
Cu	0.010	0.012-0.360	0.110 ± 0.094	0.012-0.300	14	0.061 ± 0.081	0.013-0.360	46
Fe	0.50	0.50-5.10	1.18 ± 1.15	0.58-5.10	14	1.12 ± 0.87	0.50-3.80	28
K	0.5	120-880	504 ± 179	260-880	19	493 ± 164	120-810	54
Mg	2	48-120	71 ± 14	50-93	19	70 ± 13	48-120	54
Mn	0.05	0.30-4.50	0.80 ± 0.37	0.37-1.80	19	0.76 ± 0.66	0.30-4.50	54
Mo	0.010	0.015-0.033	0.023 ± 0.001	0.022-0.023	2	0.024 ± 0.013	0.015-0.033	2
Na	1.0	3.9-74.0	20.0 ± 7.8	9.7-37.0	19	20.5 ± 15.4	3.9-74.0	54
Ni	0.010	0.010-0.082	0.018 ± 0.004	0.013-0.027	16	0.016 ± 0.011	0.010-0.082	43
Pb	0.0050	0.0050-0.0260	0.0076 ± 0.0018	0.0056-0.0120	11	0.0081 ± 0.0039	0.0050-0.0260	30
Sb	0.002	0.003-0.016	0.016	0.016	1	0.003	0.003	1
Se	0.0050	0.0051-0.0100	0.0078 ± 0.0014	0.0066-0.0094	3	0.0063 ± 0.0013	0.0051-0.0100	17
Sn	0.0050	0.0061-0.0075	-	-	-	0.0068 ± 0.0010	0.0061-0.0075	2
Sr	0.01	0.09-0.65	0.32 ± 0.07	0.18-0.40	19	0.24 ± 0.09	0.09-0.65	54
Tl	0.0020	0.0026	-	-	-	0.0026	0.0026	1
U	0.00050	0.00060-0.00160	0.00060	0.00060	1	0.00108 ± 0.00045	0.00078-0.00160	3
V	0.010	0.012-0.120	0.084 ± 0.024	0.063-0.110	3	0.046 ± 0.037	0.012-0.120	8
Zn	0.05	0.36-2.60	0.92 ± 0.35	0.36-1.60	19	0.92 ± 0.40	0.37-2.60	54

†Indicates elements analyzed by ICP-OES; all B analysis.

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Table 4. Spearman correlation matrix for metals in Niagara region sparkling wines (*n* = 73) present >LOD in all samples.

	B	Ca	Mg	Mn	K	Na	Sr	Zn
B								
Ca	-0.214							
Mg	-0.092	0.158						
Mn	0.102	**0.276** ^{a}	**0.318** ^{ab}					
K	**0.267** ^{a}	-0.015	0.150	**0.293** ^{a}				
Na	0.086	0.220	**-0.250** ^{a}	0.047	0.005			
Sr	-0.221	0.141	**0.372** ^{ab}	0.174	-0.111	0.131		
Zn	-0.054	0.038	0.214	**0.384** ^{abc}	0.159	-0.022	-0.031	

Significant at $p <$ (a) 0.05, (b) 0.01 and (c) < 0.001.

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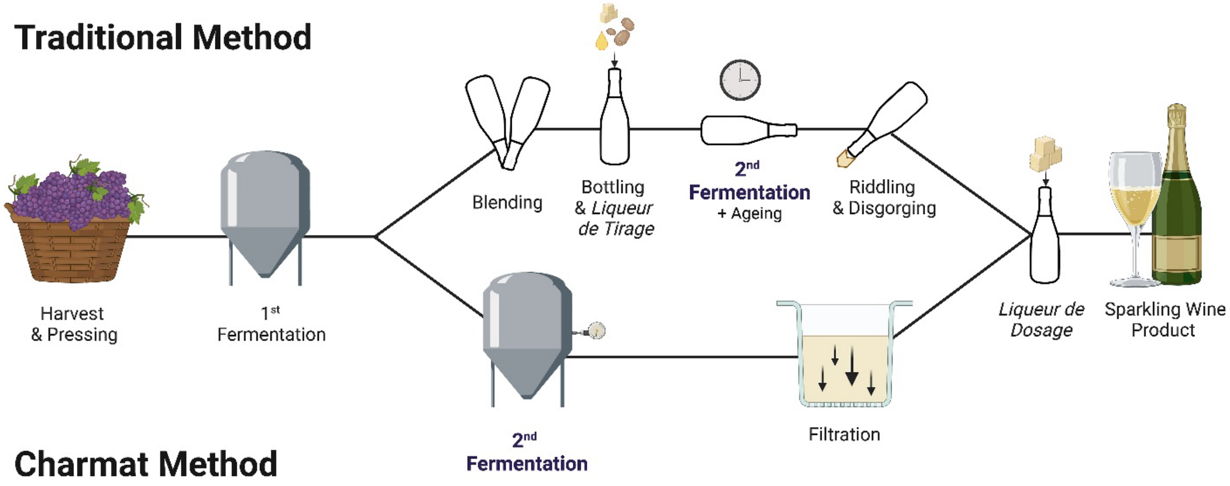

Figure 1. Overview of sparkling wine production processes for Traditional method and Charmat method wines.

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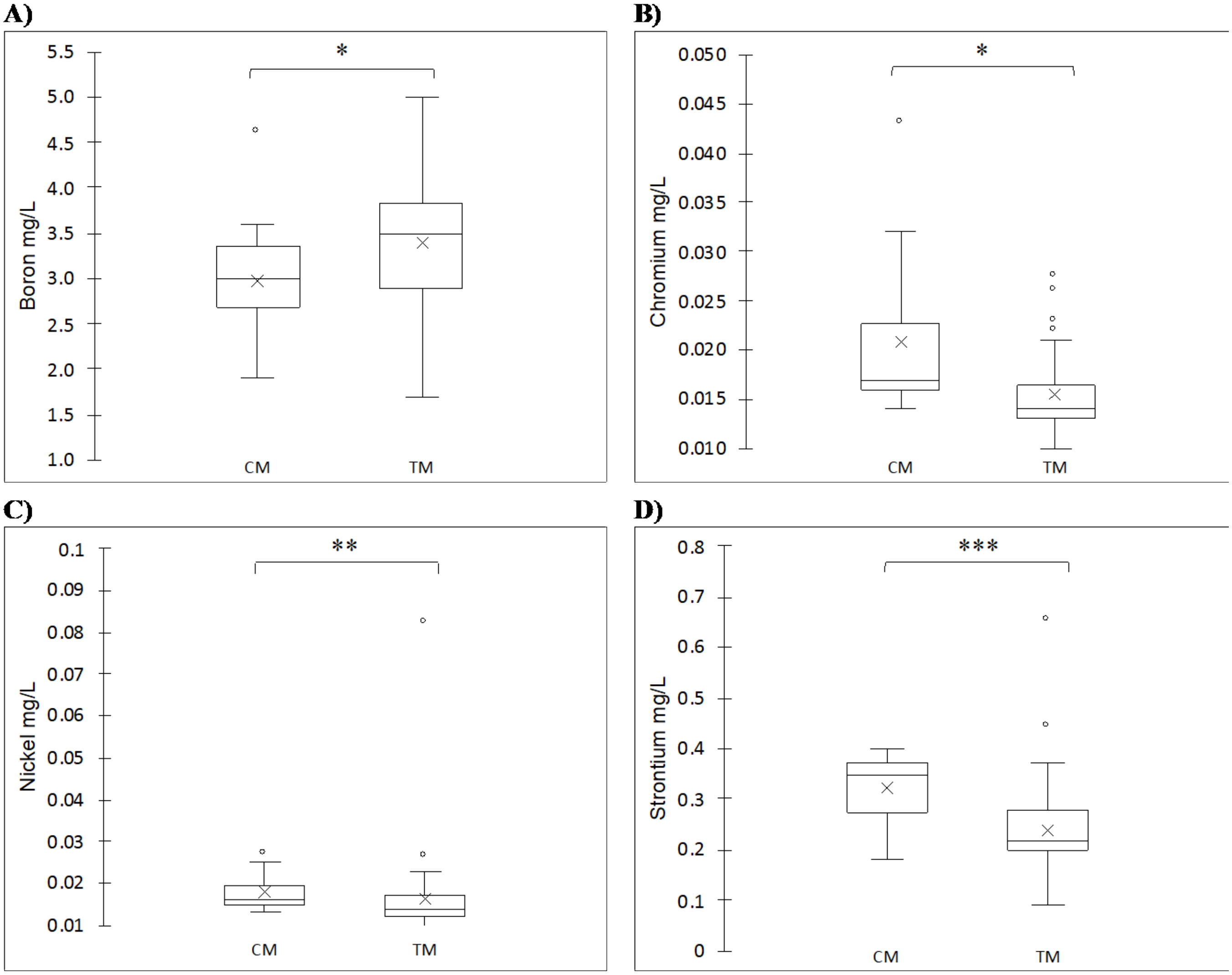

Figure 2. Box and whisker plots of statistically significant metal levels (mg/L) comparing Charmat method (CM) and Traditional method (TM) production techniques: **A**) Boron $p < 0.05$ (CM = 19 wines, TM = 54 wines); **B**) Chromium $p < 0.05$ (CM = 14 wines, TM = 35 wines); **C**) Nickel $p < 0.01$ (CM = 16 wines, TM = 43 wines); **D**) Strontium $p < 0.001$ (CM = 19 wines, TM = 54 wines). Upper and lower edges of boxes represent interquartile range from 25th to 75th percentile, respectively; internal horizontal line represents the median, and cross indicates the mean. Whiskers above and below boxes extend to maximum and minimum values, respectively, with calculated outliers identified as open circular data points. Boron concentrations were assessed using one-way ANOVA on the complete data set (zero <LOD values; normal distribution, Shapiro-Wilks test). Concentrations of other elements were evaluated by Kruskal-Wallis tests, which compares mean rank. Significance for all statistical evaluations established at $p = 0.05$.

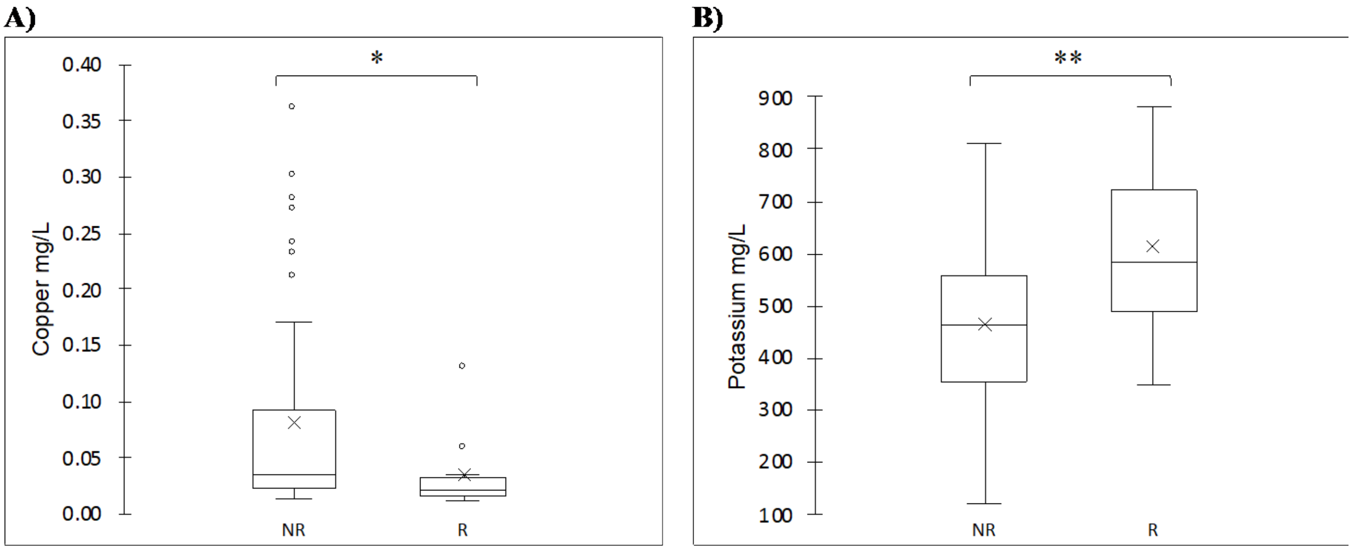

Figure 3. Box and whisker plots of statistically significant metal levels (mg/L) comparing non-rosé (NR) and rosé (R) sparkling wine styles. **A**) Copper $p < 0.05$ (NR = 50 wines, R = 10 wines); **B**) Potassium $p < 0.01$ (NR = 58 wines, R = 15 wines). Upper and lower edges of boxes represent interquartile range from 25th to 75th percentile, respectively; internal horizontal line represents the median, and cross indicates the mean. Whiskers above and below boxes extend to maximum and minimum values, respectively, with calculated outliers identified as open circular data points. Potassium was present in all wine samples although non-normally distributed (Shapiro-Wilks test). Statistical significance for all elements were evaluated by Kruskal-Wallis tests, indicating differences in mean rank, with significance established at $p = 0.05$.

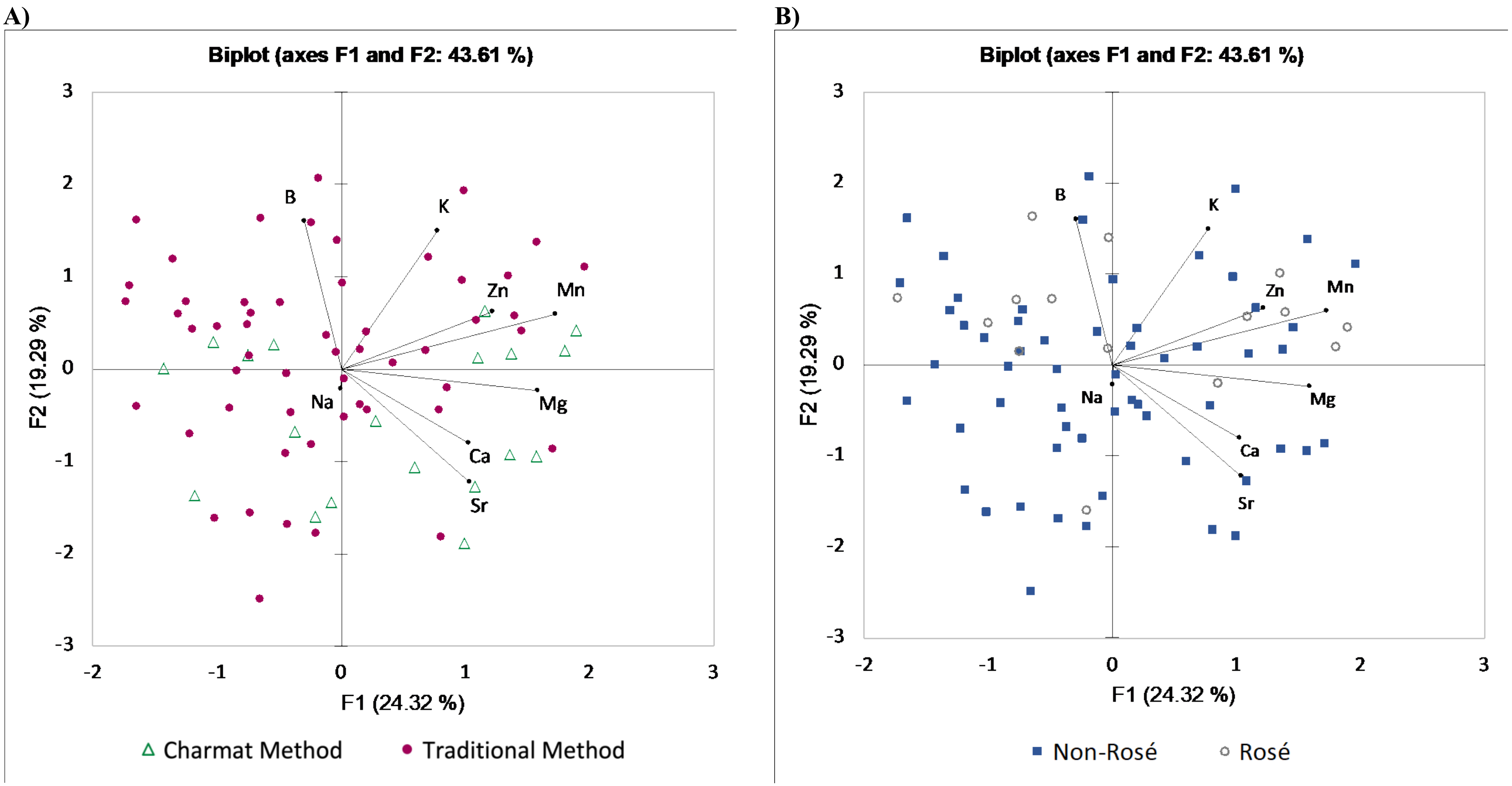

Figure 4. Principal component analysis biplot of first two principal components for metal content of sparkling wines (only elements with concentrations > LOD in all wines included *n* = 73) according to production method (Figure 4a) and style (Figure 4b).

American Journal of Enology and Viticulture (AJEV). doi: 10.5344/ajev.2022.21051

Supplementary Materials for:

Production method and wine style influences metal profiles in sparkling wines.

Table of Contents

Abbreviations Used

Ag, Silver
Al, Aluminum
As, Arsenic
B, Boron
Ba, Barium
Be, Beryllium
Ca, Calcium
Cd, Cadmium
Co, Cobalt
Cr, Chromium
Cu, Copper
Fe, Iron
K, Potassium
Mg, Magnesium
Mn, Manganese
Mo, Molybdenum
Na, Sodium
Ni, Nickel
Pb, Lead
Sb, Antimony
Se, Selenium
Sn, Tin
Sr, Strontium
Ti, Titanium
Tl, Thallium
U, Uranium
V, Vanadium
Zn, Zinc

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Table S1. Internationally regulated maximum acceptable levels for metal content in wine by the International Organization of Vine and Wine (2015).

Metal	Maximum Acceptable Level (mg/L)
Ag	<0.1
As	0.2
B	80
Br	1
Cd	0.01
Cu	1
Na	80
Pb	0.15
Zn	5

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Table S2. Sample information pertaining to production method (Charmat method – C; Traditional method – T), style (non-rosé – N; rosé – R), closure (cork or crown cap) and vintage.

Sample ID	Method	Style	Closure	Vintage
1	C	N	Crown	2018
2	C	N	Crown	2017
3	C	N	Crown	2018
4	C	N	Crown	2017
5	C	N	Cork	2017
6	C	N	Crown	NV
7	C	N	Cork	2018
8	C	N	Cork	NV
9	C	N	Cork	2019
10	C	N	Cork	2016
11	C	N	Cork	2012
12	C	N	Cork	NV
13	C	N	Cork	2013
14	C	N	Cork	2013
15	C	N	Cork	NV
16	C	R	Cork	NV
17	C	R	Cork	NV
18	C	R	Cork	2016
19	C	R	Cork	2017
20	T	N	Cork	2016
21	T	N	Cork	2016
22	T	N	Cork	NV
23	T	N	Cork	2006
24	T	N	Crown	2006
25	T	N	Crown	NV
26	T	N	Cork	2013
27	T	N	Crown	2017
28	T	N	Cork	2015
29	T	N	Cork	NV
30	T	N	Cork	2015
31	T	N	Cork	2013
32	T	N	Cork	NV
33	T	N	Cork	NV
34	T	N	Cork	NV
35	T	N	Cork	2014
36	T	N	Cork	2016
37	T	N	Cork	2016
38	T	N	Cork	NV
39	T	N	Cork	NV
40	T	N	Cork	2014
41	T	N	Cork	2012

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Sample ID	Method	Style	Closure	Vintage
42	T	N	Cork	2015
43	T	N	Cork	2017
44	T	N	Cork	NV
45	T	N	Crown	2017
46	T	N	Cork	2017
47	T	N	Cork	2006
48	T	N	Crown	2019
49	T	N	Crown	NV
50	T	N	Cork	2006
51	T	N	Cork	NV
52	T	N	Cork	2011
53	T	N	Cork	NV
54	T	N	Cork	2013
55	T	N	Cork	NV
56	T	N	Cork	NV
57	T	N	Cork	2010
58	T	N	Cork	2017
59	T	N	Crown	2018
60	T	N	Cork	2012
61	T	N	Cork	2012
62	T	N	Cork	NV
63	T	R	Crown	2016
64	T	R	Cork	2016
65	T	R	Crown	2015
66	T	R	Cork	2015
67	T	R	Cork	NV
68	T	R	Crown	2015
69	T	R	Cork	2015
70	T	R	Cork	NV
71	T	R	Cork	NV
72	T	R	Cork	NV
73	T	R	Cork	NV

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Table S3. Multi-element calibration standards for ICP-MS.

Standard-1	Standard-2A	Standard-3	Standard-4
Ce	Ag	Au	B
Dy	Al	Hf	Ge
Er	As	Ir	Mo
Eu	Ba	Pd	Nb
Gd	Be	Pt	P
Ho	Ca	Rh	Re
La	Cd	Ru	S
Lu	Co	Sb	Si
Nd	Cr	Sn	Sn
Pr	Cs	Te	Ta
Sc	Cu		Ti
Sm	Fe		W
Tb	Ga		Zr
Th	K		
Tm	Li		
Y	Mg		
Yb	Mn		
	Na		
	Ni		
	Pb		
	Rb		
	Se		
	Sr		
	Tl		
	U		
	V		
	Zn		

Table S4. Determined metal concentrations (mg/L) in 73 sparkling wines produced in Canada’s Niagara Peninsula by ICP-MS and ICP-OES.

Sample ID	Al	Sb	As	Ba	Be	B†	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Mo	Ni	K	Se	Na	Sr	Tl	Sn	U	V	Zn
1	0.20	n.d.	0.054	0.039	0.0013	1.9	0.00016	53	0.017	n.d.	0.230	n.d.	n.d.	89	1.10	n.d.	0.015	370	0.0074	15.0	0.35	n.d.	n.d.	n.d.	n.d.	1.60
2	0.09	n.d.	0.013	0.025	n.d.	3.1	0.00010	59	n.d.	n.d.	n.d.	n.d.	n.d.	51	0.65	n.d.	n.d.	490	n.d.	29.0	0.19	n.d.	n.d.	n.d.	n.d.	0.73
3	0.19	n.d.	0.016	0.037	0.0011	2.0	0.00014	56	0.017	n.d.	0.230	n.d.	n.d.	93	1.10	n.d.	0.015	390	n.d.	16.0	0.37	n.d.	n.d.	n.d.	n.d.	1.60
4	0.37	n.d.	0.012	0.039	n.d.	3.3	0.00014	64	n.d.	n.d.	0.018	0.64	n.d.	54	0.52	n.d.	n.d.	260	n.d.	23.0	0.35	n.d.	n.d.	n.d.	0.063	0.36
5	n.d.	n.d.	0.045	0.018	n.d.	2.7	n.d.	52	0.018	n.d.	0.160	0.72	n.d.	51	0.75	n.d.	0.014	480	0.0094	9.7	0.22	n.d.	n.d.	n.d.	n.d.	0.96
6	2.00	n.d.	0.034	0.065	0.0064	3.2	0.00041	79	0.032	n.d.	0.094	1.30	0.0120	65	0.65	n.d.	0.025	350	0.0066	31.0	0.34	n.d.	n.d.	n.d.	n.d.	0.54
7	n.d.	n.d.	0.014	0.036	0.0011	3.0	n.d.	66	0.019	n.d.	0.017	1.00	0.0062	81	0.49	n.d.	0.016	590	n.d.	15.0	0.29	n.d.	n.d.	n.d.	n.d.	0.63
8	0.72	n.d.	0.013	0.054	0.0018	2.4	n.d.	92	0.016	n.d.	0.019	0.75	0.0083	93	0.58	n.d.	0.017	490	n.d.	19.0	0.39	n.d.	n.d.	n.d.	n.d.	0.52
9	n.d.	n.d.	0.012	0.044	n.d.	3.4	n.d.	87	n.d.	n.d.	0.038	n.d.	n.d.	89	0.64	n.d.	0.013	750	n.d.	21.0	0.26	n.d.	n.d.	n.d.	n.d.	1.00
10	0.70	n.d.	0.014	0.035	n.d.	3.5	n.d.	58	0.043	n.d.	0.120	0.98	0.0064	62	0.40	n.d.	0.027	370	n.d.	20.0	0.40	n.d.	n.d.	0.00060	n.d.	1.10
11	0.58	n.d.	0.015	0.049	0.0017	3.6	0.00010	74	n.d.	n.d.	0.140	0.58	0.0080	66	0.96	n.d.	0.015	540	n.d.	14.0	0.36	n.d.	n.d.	n.d.	n.d.	1.10
12	n.d.	n.d.	0.014	0.019	n.d.	2.7	n.d.	68	0.016	n.d.	0.029	0.85	0.0056	66	1.20	n.d.	0.016	320	n.d.	13.0	0.31	n.d.	n.d.	n.d.	n.d.	0.92
13	0.61	n.d.	0.014	0.035	0.0011	2.3	0.00015	69	0.014	n.d.	n.d.	1.20	0.0085	73	1.10	n.d.	0.015	470	n.d.	17.0	0.37	n.d.	n.d.	n.d.	n.d.	0.80
14	0.68	n.d.	n.d.	0.022	n.d.	2.7	n.d.	45	n.d.	n.d.	0.300	n.d.	n.d.	50	0.38	n.d.	n.d.	330	n.d.	13.0	0.18	n.d.	n.d.	n.d.	n.d.	1.30
15	0.97	0.016	0.029	0.041	0.0012	4.6	0.00023	68	0.015	n.d.	n.d.	5.10	0.0077	74	1.20	0.022	0.017	650	n.d.	35.0	0.36	n.d.	n.d.	n.d.	0.110	0.78
16	0.69	n.d.	0.020	0.055	0.0037	3.5	0.00011	86	0.027	n.d.	n.d.	0.98	0.0066	74	0.81	n.d.	0.020	810	n.d.	22.0	0.38	n.d.	n.d.	n.d.	n.d.	1.20
17	0.57	n.d.	0.012	0.042	n.d.	2.8	n.d.	65	0.024	n.d.	0.012	0.60	0.0059	60	0.50	n.d.	0.016	680	n.d.	16.0	0.21	n.d.	n.d.	n.d.	n.d.	0.55
18	0.53	n.d.	0.011	0.028	n.d.	2.7	0.00033	59	0.017	n.d.	0.130	1.00	n.d.	73	0.37	n.d.	0.019	350	n.d.	14.0	0.39	n.d.	n.d.	n.d.	n.d.	0.80
19	1.50	n.d.	0.030	0.120	0.0037	3.3	0.00046	69	0.014	0.0058	n.d.	0.79	0.0085	79	1.80	0.023	0.023	880	n.d.	37.0	0.35	n.d.	n.d.	n.d.	0.080	1.00
20	0.32	n.d.	0.054	0.035	n.d.	3.5	0.00012	66	0.010	n.d.	0.034	n.d.	n.d.	56	0.71	n.d.	n.d.	430	0.0100	42.0	0.12	n.d.	n.d.	n.d.	n.d.	0.87
21	0.40	n.d.	0.026	0.034	n.d.	2.7	0.00018	43	0.021	n.d.	0.031	0.97	0.0078	66	0.69	n.d.	0.023	440	0.0054	29.0	0.32	n.d.	n.d.	n.d.	n.d.	1.20
22	0.25	n.d.	0.020	0.015	n.d.	5.0	0.00013	44	0.013	n.d.	0.023	n.d.	n.d.	70	0.37	n.d.	n.d.	320	n.d.	6.4	0.09	n.d.	n.d.	n.d.	n.d.	0.64
23	0.23	n.d.	0.014	0.020	n.d.	2.2	n.d.	87	0.011	n.d.	0.210	n.d.	n.d.	64	0.30	n.d.	n.d.	200	n.d.	31.0	0.32	n.d.	n.d.	n.d.	n.d.	0.74

Sample ID	Al	Sb	As	Ba	Be	B†	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Mo	Ni	K	Se	Na	Sr	Tl	Sn	U	V	Zn
24	0.19	n.d.	0.016	0.046	n.d.	3.3	0.00018	58	0.013	n.d.	0.034	n.d.	0.0062	75	0.38	n.d.	0.014	380	n.d.	9.9	0.21	n.d.	n.d.	n.d.	n.d.	0.50
25	0.27	n.d.	0.016	0.030	n.d.	2.0	0.00012	70	n.d.	n.d.	0.170	n.d.	n.d.	63	0.31	n.d.	n.d.	260	n.d.	31.0	0.25	n.d.	n.d.	n.d.	n.d.	1.40
26	0.74	n.d.	0.014	0.064	0.0027	3.9	0.00012	74	0.016	n.d.	0.028	3.00	0.0080	83	2.40	n.d.	0.014	720	n.d.	15.0	0.28	n.d.	n.d.	n.d.	n.d.	1.30
27	0.99	n.d.	0.014	0.020	n.d.	3.9	0.00031	78	0.016	n.d.	0.240	0.96	0.0054	67	0.81	n.d.	n.d.	210	n.d.	17.0	0.24	n.d.	n.d.	n.d.	n.d.	0.68
28	0.93	n.d.	0.012	0.030	n.d.	3.7	0.00036	57	0.016	n.d.	0.360	0.94	0.0074	62	0.74	n.d.	n.d.	310	n.d.	15.0	0.23	n.d.	n.d.	n.d.	n.d.	0.67
29	0.11	n.d.	n.d.	n.d.	n.d.	3.8	0.00013	72	0.012	n.d.	0.015	n.d.	n.d.	86	0.59	n.d.	0.013	120	n.d.	7.4	0.19	n.d.	n.d.	n.d.	n.d.	0.92
30	0.57	n.d.	0.037	0.025	n.d.	3.3	n.d.	44	0.013	n.d.	0.019	0.60	0.0066	55	0.32	n.d.	0.011	610	0.0080	13.0	0.17	n.d.	n.d.	n.d.	n.d.	1.10
31	0.62	n.d.	0.042	0.039	n.d.	2.5	n.d.	54	0.022	n.d.	n.d.	0.81	0.0093	71	0.77	n.d.	0.021	480	0.0083	32.0	0.32	n.d.	n.d.	n.d.	n.d.	1.40
32	0.96	n.d.	0.031	0.045	0.0030	3.6	n.d.	65	0.015	n.d.	0.015	n.d.	0.0073	66	0.35	n.d.	0.011	500	0.0059	25.0	0.22	n.d.	n.d.	n.d.	n.d.	0.83
33	n.d.	n.d.	0.031	0.019	n.d.	3.0	n.d.	63	n.d.	n.d.	0.017	n.d.	n.d.	75	1.30	n.d.	0.012	530	0.0058	13.0	0.15	n.d.	n.d.	n.d.	n.d.	1.50
34	2.20	n.d.	0.031	0.048	0.0030	4.7	n.d.	65	0.017	n.d.	0.061	n.d.	0.0079	62	0.33	n.d.	0.013	440	0.0070	43.0	0.18	n.d.	n.d.	n.d.	n.d.	0.94
35	0.84	n.d.	0.029	0.039	0.0019	4.3	n.d.	58	0.014	n.d.	0.053	n.d.	0.0062	55	0.41	n.d.	0.011	540	0.0057	22.0	0.24	n.d.	n.d.	n.d.	n.d.	0.52
36	0.66	n.d.	0.029	0.036	n.d.	3.9	0.00022	36	0.014	n.d.	0.032	0.64	n.d.	52	0.45	n.d.	0.014	620	0.0054	11.0	0.19	n.d.	n.d.	n.d.	0.019	0.66
37	0.61	n.d.	0.022	0.030	n.d.	3.2	0.00020	65	n.d.	n.d.	0.030	n.d.	n.d.	65	0.43	n.d.	0.016	530	n.d.	8.0	0.24	n.d.	n.d.	n.d.	n.d.	0.85
38	n.d.	n.d.	0.026	0.030	n.d.	3.0	n.d.	66	n.d.	n.d.	0.039	n.d.	n.d.	80	0.45	n.d.	0.014	340	n.d.	7.1	0.21	n.d.	n.d.	n.d.	0.012	1.30
39	0.53	n.d.	0.021	0.026	n.d.	2.5	0.00027	86	0.018	n.d.	0.015	0.50	0.0063	99	0.86	n.d.	0.017	470	0.0051	7.2	0.28	n.d.	n.d.	n.d.	n.d.	1.10
40	0.61	n.d.	0.025	0.025	n.d.	3.4	n.d.	37	0.014	n.d.	0.029	n.d.	0.0066	71	0.35	n.d.	0.011	380	0.0052	17.0	0.29	n.d.	n.d.	n.d.	n.d.	0.39
41	0.84	n.d.	0.024	0.023	n.d.	3.9	n.d.	40	0.014	n.d.	0.045	0.77	0.0110	58	0.33	n.d.	n.d.	380	n.d.	24.0	0.37	n.d.	n.d.	n.d.	n.d.	0.48
42	0.62	n.d.	0.023	0.044	n.d.	3.7	n.d.	75	0.013	n.d.	0.040	n.d.	n.d.	64	0.80	n.d.	n.d.	540	0.0052	48.0	0.13	n.d.	n.d.	n.d.	n.d.	0.93
43	0.82	n.d.	0.034	0.034	n.d.	3.6	n.d.	42	n.d.	n.d.	0.270	n.d.	n.d.	72	0.52	n.d.	0.026	390	0.0068	13.0	0.27	n.d.	n.d.	n.d.	n.d.	1.30
44	0.68	n.d.	0.027	0.043	n.d.	2.9	n.d.	48	0.014	n.d.	0.089	n.d.	0.0051	68	0.60	n.d.	0.012	630	n.d.	28.0	0.17	n.d.	n.d.	n.d.	n.d.	0.51
45	1.00	n.d.	0.021	0.042	0.0036	3.1	n.d.	55	0.017	n.d.	0.052	2.10	0.0096	79	0.55	n.d.	0.018	460	n.d.	13.0	0.24	n.d.	n.d.	n.d.	n.d.	0.42
46	0.59	n.d.	0.017	0.021	n.d.	3.6	0.00024	73	n.d.	n.d.	0.022	n.d.	0.0056	73	0.66	n.d.	0.013	390	n.d.	64.0	0.17	n.d.	n.d.	n.d.	n.d.	0.97
47	0.96	n.d.	0.014	0.039	0.0020	3.1	n.d.	78	n.d.	n.d.	0.086	n.d.	0.0066	57	0.83	n.d.	0.010	500	n.d.	24.0	0.22	n.d.	n.d.	n.d.	n.d.	1.10

Sample ID	Al	Sb	As	Ba	Be	B[†]	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Mo	Ni	K	Se	Na	Sr	Tl	Sn	U	V	Zn
48	0.82	n.d.	0.020	0.041	n.d.	1.7	n.d.	72	n.d.	n.d.	0.026	0.72	n.d.	67	0.33	n.d.	n.d.	560	n.d.	9.0	0.22	n.d.	n.d.	n.d.	0.048	0.67
49	n.d.	n.d.	0.014	0.019	n.d.	4.6	0.00025	62	0.028	n.d.	0.026	0.58	n.d.	66	0.55	n.d.	0.015	750	n.d.	74.0	0.20	n.d.	0.0075	n.d.	n.d.	0.95
50	0.78	n.d.	0.018	0.041	n.d.	2.1	n.d.	77	n.d.	n.d.	0.016	0.65	n.d.	65	0.36	n.d.	n.d.	330	n.d.	12.0	0.21	n.d.	n.d.	n.d.	0.074	0.49
51	5.20	0.003	0.037	0.041	0.0039	2.5	0.00031	82	0.014	n.d.	0.014	1.90	0.0071	70	1.10	0.033	0.011	240	n.d.	69.0	0.31	n.d.	n.d.	0.00160	0.120	0.81
52	0.51	n.d.	0.011	0.045	n.d.	2.8	0.00022	68	0.023	n.d.	0.280	n.d.	0.0260	66	0.79	n.d.	0.018	810	n.d.	15.0	0.15	n.d.	n.d.	n.d.	n.d.	2.60
53	1.30	n.d.	0.011	0.060	0.0036	3.2	n.d.	64	0.012	n.d.	n.d.	n.d.	0.0058	60	0.31	n.d.	n.d.	650	n.d.	14.0	0.20	n.d.	n.d.	n.d.	n.d.	0.73
54	1.50	n.d.	0.013	0.058	0.0021	4.5	n.d.	65	0.016	n.d.	n.d.	0.86	0.0084	74	1.40	n.d.	0.014	810	n.d.	16.0	0.20	n.d.	n.d.	0.00078	n.d.	0.98
55	n.d.	n.d.	0.016	0.035	n.d.	3.7	n.d.	70	n.d.	n.d.	0.016	0.72	n.d.	90	1.30	n.d.	0.014	620	n.d.	13.0	0.20	n.d.	n.d.	n.d.	n.d.	1.50
56	0.97	n.d.	0.012	0.056	0.0037	2.0	n.d.	92	n.d.	n.d.	n.d.	0.53	0.0138	62	0.44	n.d.	0.010	315	n.d.	15.0	0.20	n.d.	n.d.	n.d.	n.d.	0.73
57	0.72	n.d.	0.025	0.025	n.d.	2.9	0.00028	55	n.d.	n.d.	0.041	3.80	n.d.	76	0.59	n.d.	0.014	400	n.d.	5.6	0.29	n.d.	n.d.	n.d.	n.d.	0.43
58	0.83	n.d.	0.021	0.024	0.0010	3.5	0.00024	68	0.026	n.d.	n.d.	0.58	0.0056	61	1.10	n.d.	0.022	560	n.d.	21.0	0.24	n.d.	n.d.	n.d.	n.d.	0.76
59	0.76	n.d.	0.026	0.082	0.0019	3.5	0.00020	58	0.016	n.d.	0.014	1.20	0.0089	98	0.73	n.d.	0.019	710	0.0058	12.0	0.44	n.d.	0.0061	n.d.	0.020	1.10
60	1.70	n.d.	0.016	0.034	n.d.	3.7	0.00031	70	0.012	0.0060	0.042	3.00	0.0077	69	1.80	n.d.	0.082	610	n.d.	24.0	0.30	n.d.	n.d.	n.d.	n.d.	0.37
61	1.60	n.d.	0.030	0.058	0.0027	2.6	0.00023	74	0.020	n.d.	0.028	0.81	0.0053	68	0.52	0.015	0.014	270	n.d.	15.0	0.28	n.d.	n.d.	0.00087	0.055	0.65
62	0.57	n.d.	0.013	0.019	n.d.	4.9	n.d.	56	n.d.	n.d.	0.028	n.d.	n.d.	53	4.50	n.d.	0.012	400	n.d.	11.0	0.10	n.d.	n.d.	n.d.	n.d.	1.70
63	0.19	n.d.	0.025	0.022	n.d.	3.5	n.d.	47	0.014	n.d.	n.d.	0.53	n.d.	95	0.52	n.d.	0.020	465	n.d.	13.0	0.23	n.d.	n.d.	n.d.	n.d.	0.84
64	0.10	n.d.	0.020	0.025	n.d.	3.0	0.00011	58	n.d.	n.d.	n.d.	n.d.	0.0057	87	1.50	n.d.	0.012	660	n.d.	3.9	0.28	0.0026	n.d.	n.d.	n.d.	0.95
65	0.25	n.d.	0.017	0.029	n.d.	3.8	0.00012	51	n.d.	n.d.	0.023	0.53	n.d.	67	0.49	n.d.	0.014	480	n.d.	12.0	0.22	n.d.	n.d.	n.d.	n.d.	0.81
66	0.65	n.d.	0.032	0.031	n.d.	4.1	n.d.	44	n.d.	n.d.	0.035	n.d.	0.0050	56	0.40	n.d.	0.010	470	0.0061	29.0	0.21	n.d.	n.d.	n.d.	n.d.	0.60
67	0.65	n.d.	0.022	0.039	n.d.	3.6	0.00025	61	n.d.	n.d.	0.022	n.d.	n.d.	48	0.68	n.d.	0.010	500	0.0054	32.0	0.22	n.d.	n.d.	n.d.	n.d.	1.00
68	0.55	n.d.	0.016	0.043	n.d.	3.7	n.d.	54	0.011	n.d.	0.019	0.60	n.d.	74	0.54	n.d.	0.017	770	n.d.	13.0	0.21	n.d.	n.d.	n.d.	n.d.	0.89
69	0.53	n.d.	0.022	0.031	n.d.	2.7	0.00012	47	n.d.	n.d.	0.013	n.d.	0.0110	68	0.31	n.d.	0.012	620	n.d.	16.0	0.17	n.d.	n.d.	n.d.	n.d.	0.88
70	1.20	n.d.	0.027	0.049	0.0041	4.7	0.00019	58	0.014	n.d.	n.d.	1.70	0.0088	120	0.66	n.d.	0.014	550	0.0060	13.0	0.65	n.d.	n.d.	n.d.	0.018	0.97
71	n.d.	n.d.	0.015	0.023	n.d.	4.1	0.00013	62	0.011	n.d.	0.016	0.61	n.d.	59	0.78	n.d.	0.017	810	n.d.	10.0	0.20	n.d.	n.d.	n.d.	n.d.	0.46

Sample ID	Al	Sb	As	Ba	Be	B†	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Mo	Ni	K	Se	Na	Sr	Tl	Sn	U	V	Zn
72	n.d.	n.d.	0.017	0.027	n.d.	3.9	0.00013	66	n.d.	n.d.	0.017	0.69	n.d.	80	0.99	n.d.	0.013	585	n.d.	16.0	0.25	n.d.	n.d.	n.d.	n.d.	1.40
73	0.54	n.d.	0.016	0.021	n.d.	2.4	0.00013	71	0.012	n.d.	0.057	n.d.	n.d.	68	0.90	n.d.	0.017	560	n.d.	9.3	0.23	n.d.	n.d.	n.d.	n.d.	0.95

†Indicates elements analyzed by ICP-OES; all B analysis.

Table S5. Spearman correlation matrix for metals in Traditional method (TM) Niagara region sparkling wines (*n* = 54) present >LOD in all samples.

	B	Ca	Mg	Mn	K	Na	Sr	Zn
B								
Ca	**-0.312** [a]							
Mg	-0.097	0.062						
Mn	0.161	**0.276** [a]	**0.296** [a]					
K	0.205	-0.169	0.055	**0.299** [a]				
Na	0.061	0.137	**-0.377** [ab]	-0.016	-0.075			
Sr	-0.219	0.011	**0.305** [a]	0.069	-0.171	0.038		
Zn	-0.033	0.154	0.206	**0.384** [ab]	0.215	0.055	-0.106	

Significant at *p* < (a) 0.05, (b) 0.01 and (c) < 0.001.

Table S6. Spearman correlation matrix for metals in Charmat method (CM) Niagara region sparkling wines (*n* = 19) present >LOD in all samples.

	B	Ca	Mg	Mn	K	Na	Sr	Zn
B								
Ca	0.389							
Mg	-0.180	0.429						
Mn	-0.004	0.237	0.344					
K	0.415	**0.482** [a]	0.383	0.258				
Na	**0.518** [a]	0.458	0.170	0.230	0.374			
Sr	0.061	0.266	**0.474** [a]	0.084	-0.025	0.175		
Zn	-0.095	-0.337	0.188	0.265	0.053	-0.319	0.118	

Significant at *p* < (a) 0.05, (b) 0.01 and (c) < 0.001.

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Table S7. Spearman correlation matrix for metals in non-rosé Niagara region sparkling wines (*n* = 58) present >LOD in all samples.

	B	Ca	Mg	Mn	K	Na	Sr	Zn
B								
Ca	-0.194							
Mg	-0.132	0.200						
Mn	0.107	0.202	**0.322** [a]					
K	**0.274** [a]	-0.066	0.124	0.254				
Na	0.096	0.212	-0.212	0.067	0.042			
Sr	**-0.282** [a]	0.099	**0.315** [a]	0.115	-0.145	0.151		
Zn	-0.074	-0.017	0.134	**0.369** [ab]	0.161	-0.047	-0.126	

Significant at *p* < (a) 0.05, (b) 0.01 and (c) < 0.001.

Table S8. Spearman correlation matrix for metals in rosé Niagara region sparkling wines (*n* = 15) present >LOD in all samples.

	B	Ca	Mg	Mn	K	Na	Sr	Zn
B								
Ca	-0.248							
Mg	0.005	0.037						
Mn	0.048	**0.682** [ab]	0.370					
K	-0.036	**0.541** [a]	0.067	**0.559** [a]				
Na	0.047	0.135	-0.238	-0.079	0.088			
Sr	-0.050	0.386	**0.659** [ab]	0.408	-0.128	0.022		
Zn	0.014	0.469	0.476	**0.644** [a]	0.236	0.299	**0.554** [a]	

Significant at *p* < (a) 0.05, (b) 0.01 and (c) < 0.001.

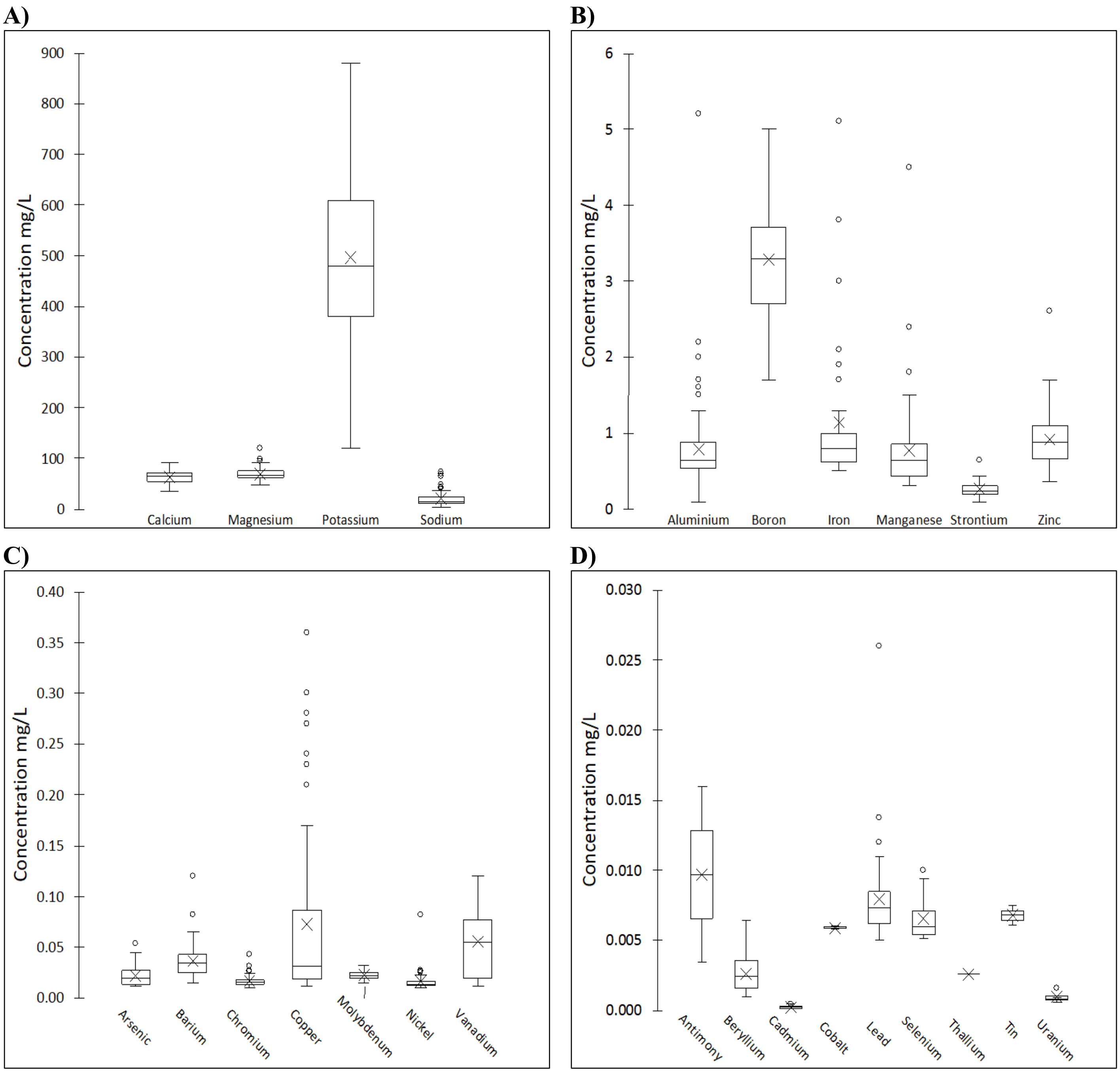

Figure S1. Box and whisker plot of all metals (*n* = 26) determined in 73 Ontario sparkling wine samples with measured amounts > LOD.

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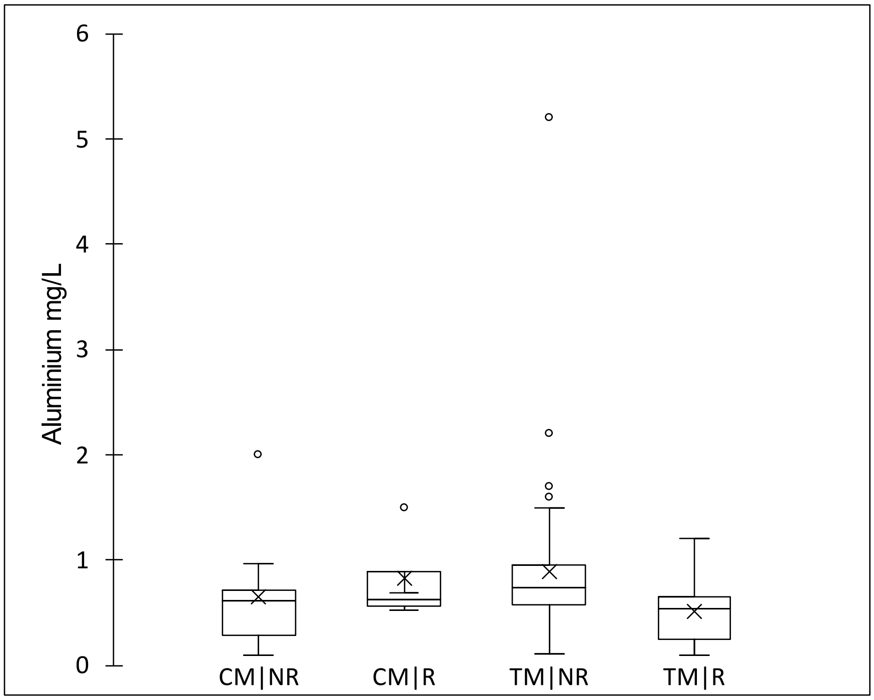

Figure S2. Box and whisker plot of Aluminum by production method and style for wines with measured amounts > LOD.

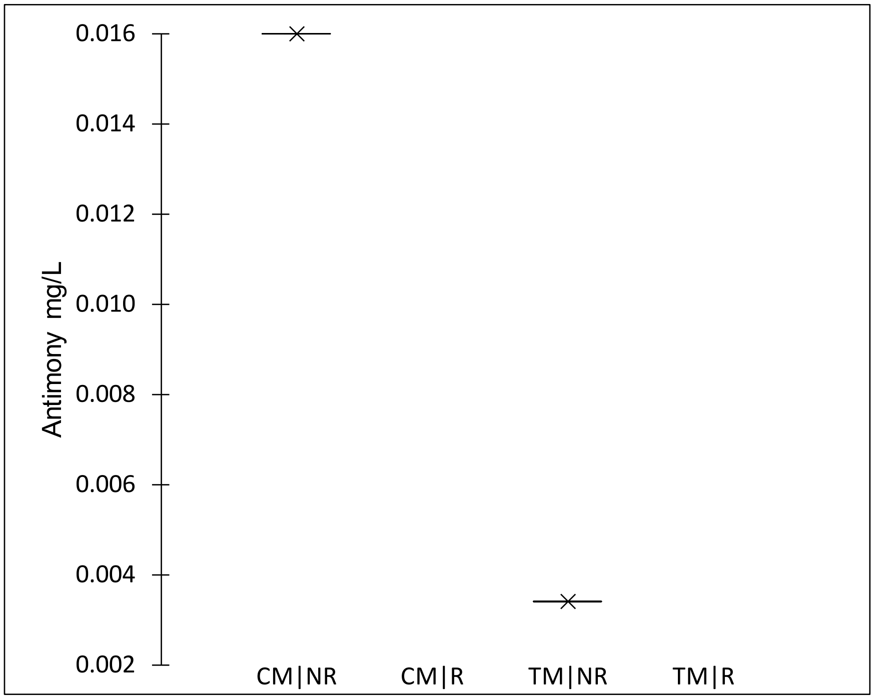

Figure S3. Box and whisker plot of Antimony by production method and style for wines with measured amounts > LOD.

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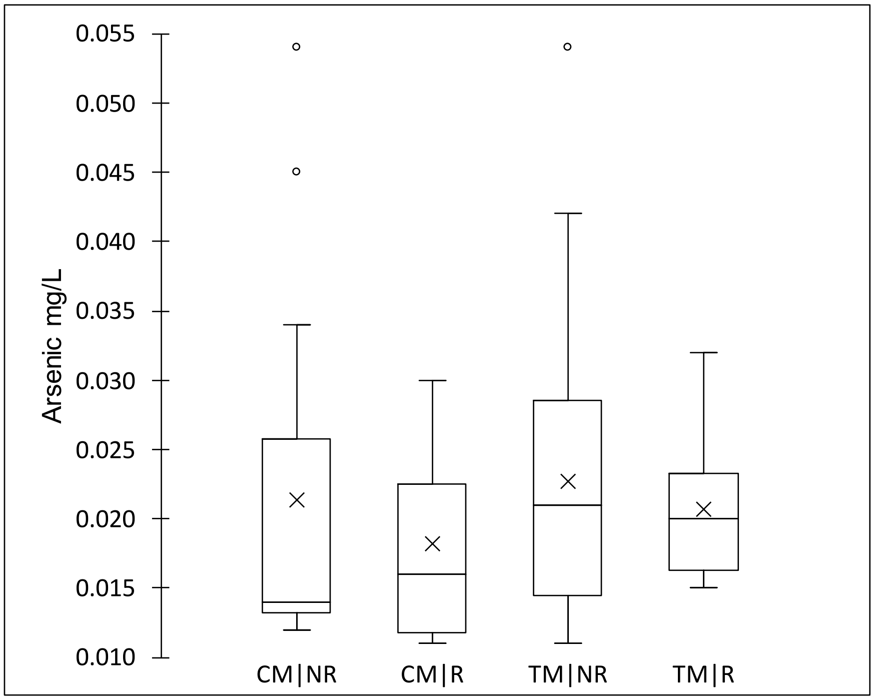

Figure S4. Box and whisker plot of Arsenic by production method and style for wines with measured amounts > LOD.

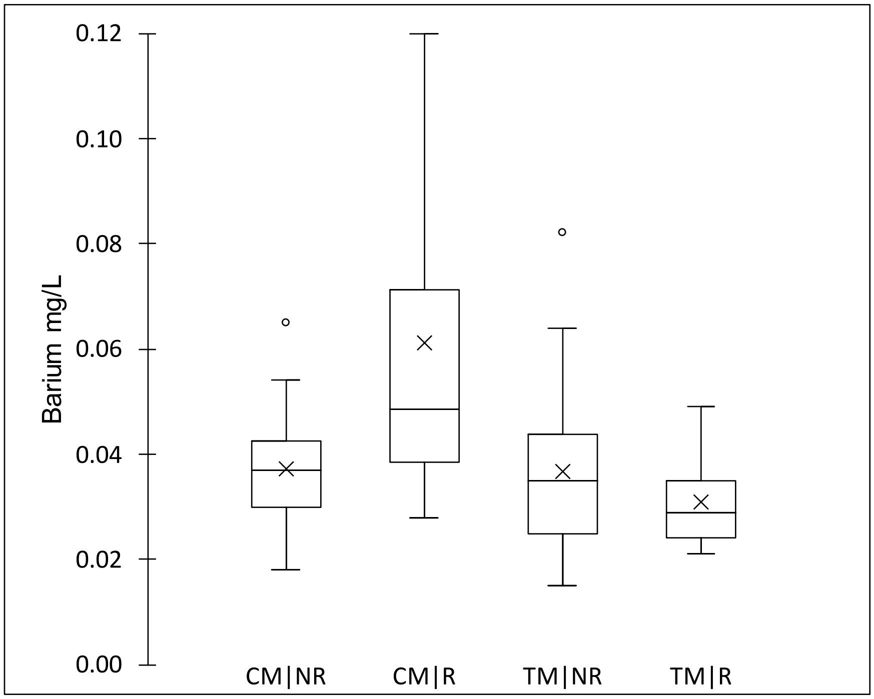

Figure S5. Box and whisker plot of Barium by production method and style for wines with measured amounts > LOD.

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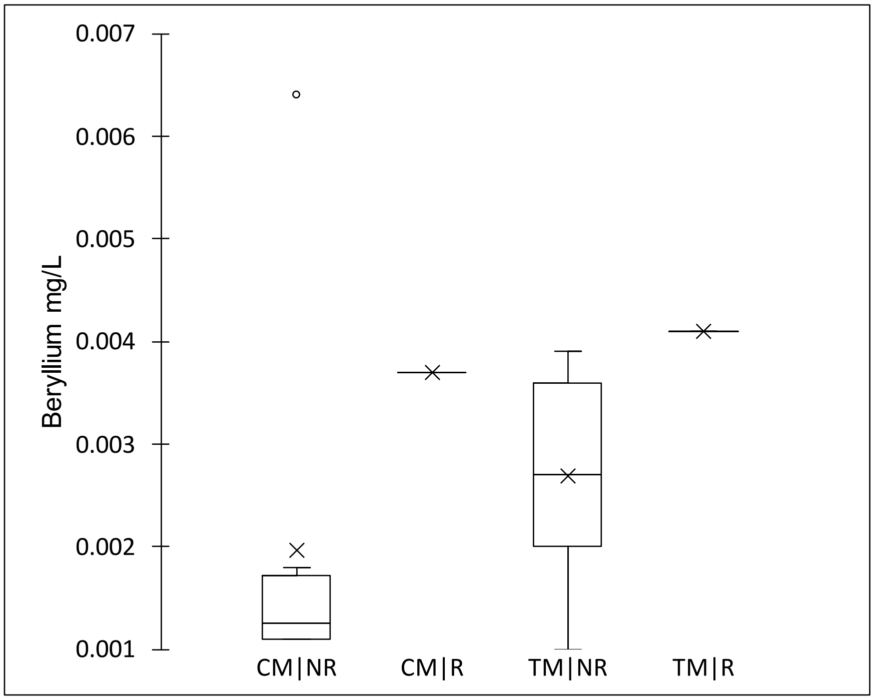

Figure S6. Box and whisker plot of Beryllium by production method and style for wines with measured amounts > LOD.

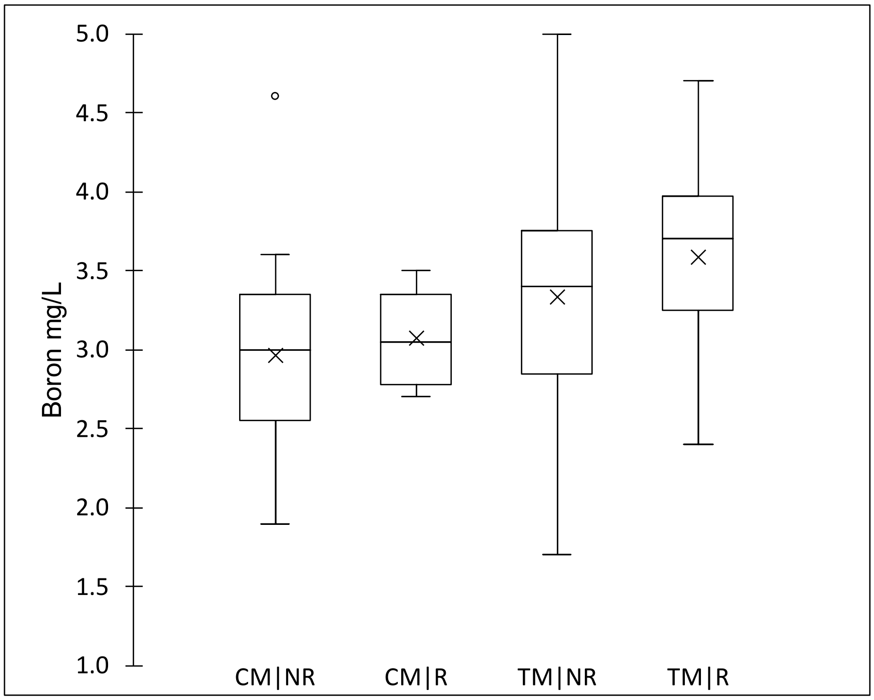

Figure S7. Box and whisker plot of Boron by production method and style for wines with measured amounts > LOD.

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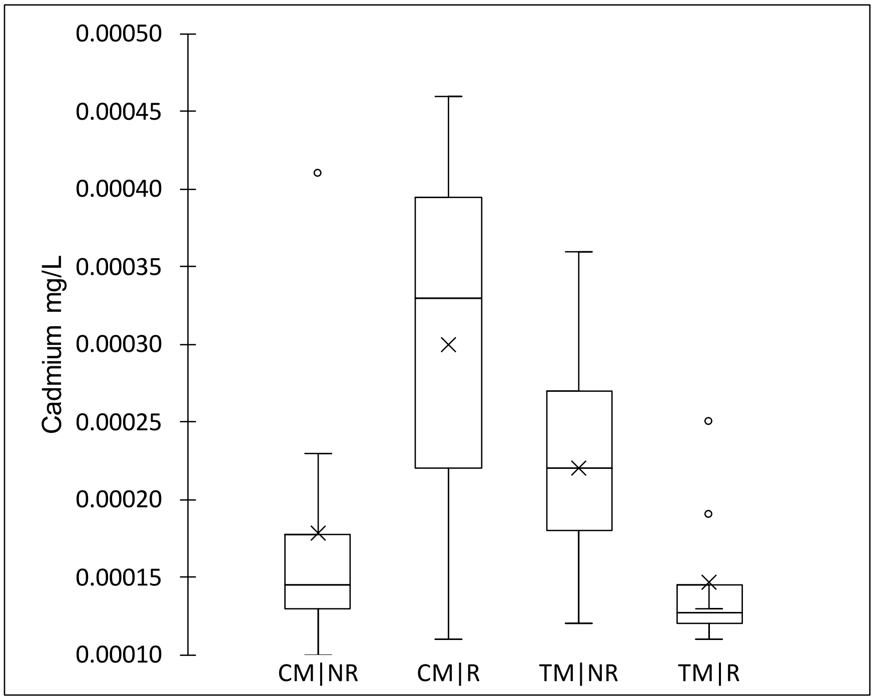

Figure S8. Box and whisker plot of Cadmium by production method and style for wines with measured amounts > LOD.

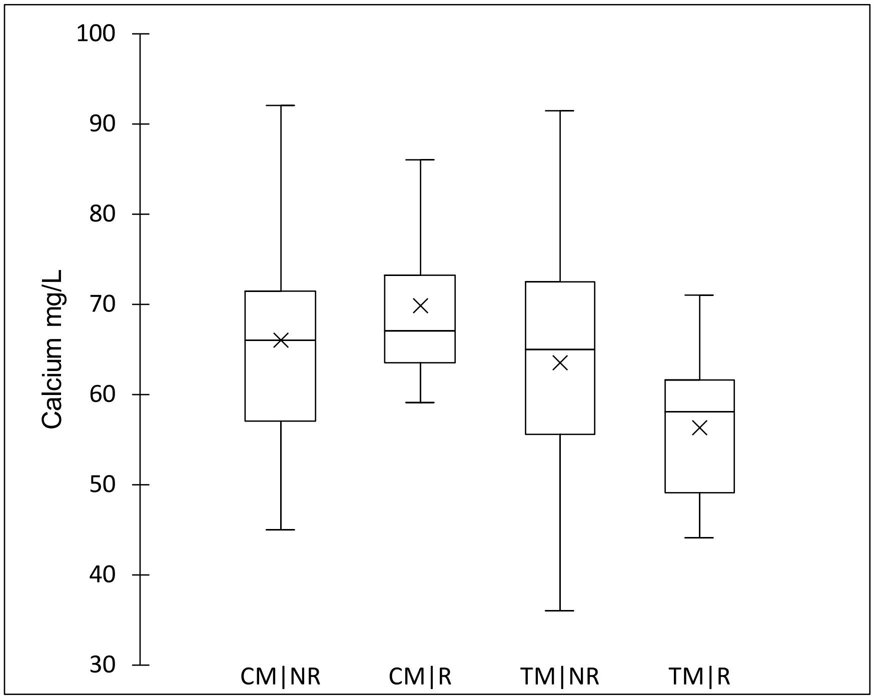

Figure S9. Box and whisker plot of Calcium by production method and style for wines with measured amounts > LOD.

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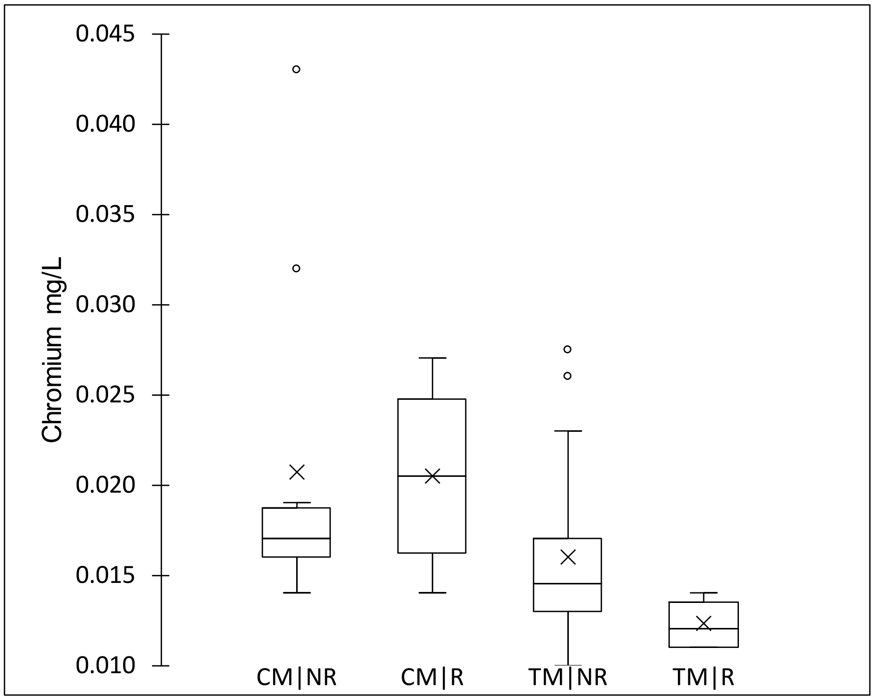

Figure S10. Box and whisker plot of Chromium by production method and style for wines with measured amounts > LOD.

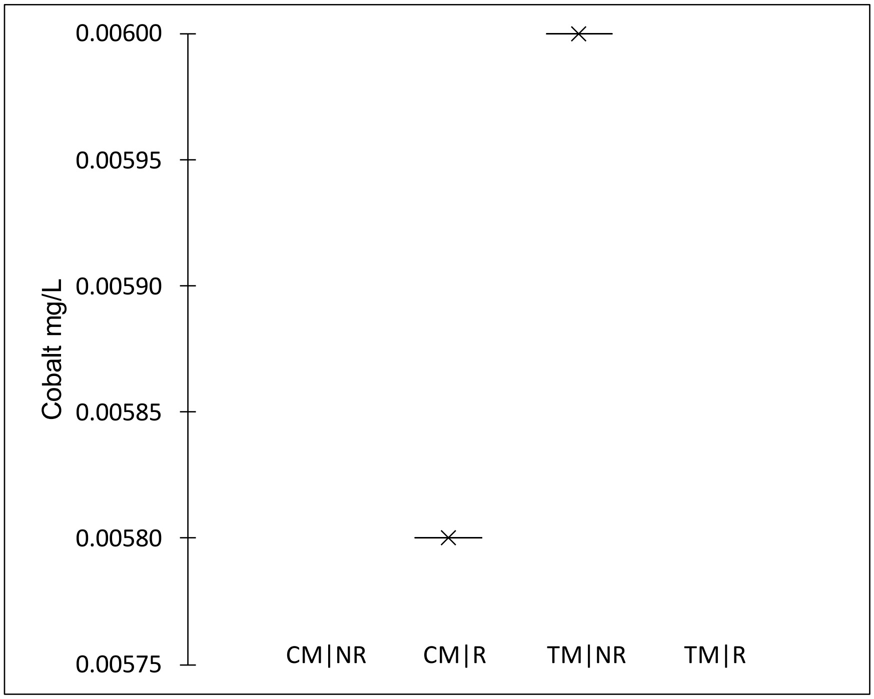

Figure S11. Box and whisker plot of Cobalt by production method and style for wines with measured amounts > LOD.

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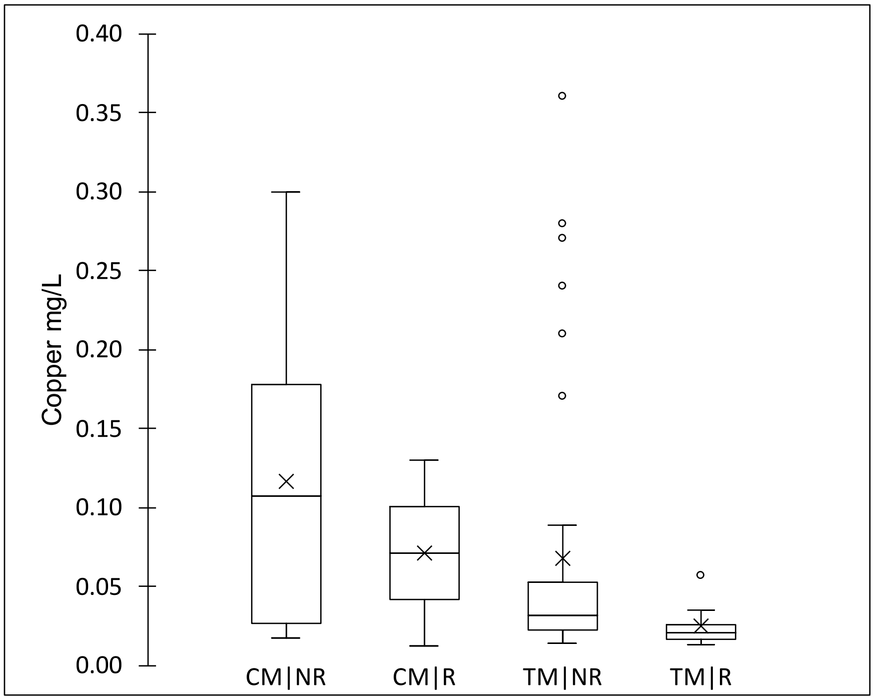

Figure S12. Box and whisker plot of Copper by production method and style for wines with measured amounts > LOD.

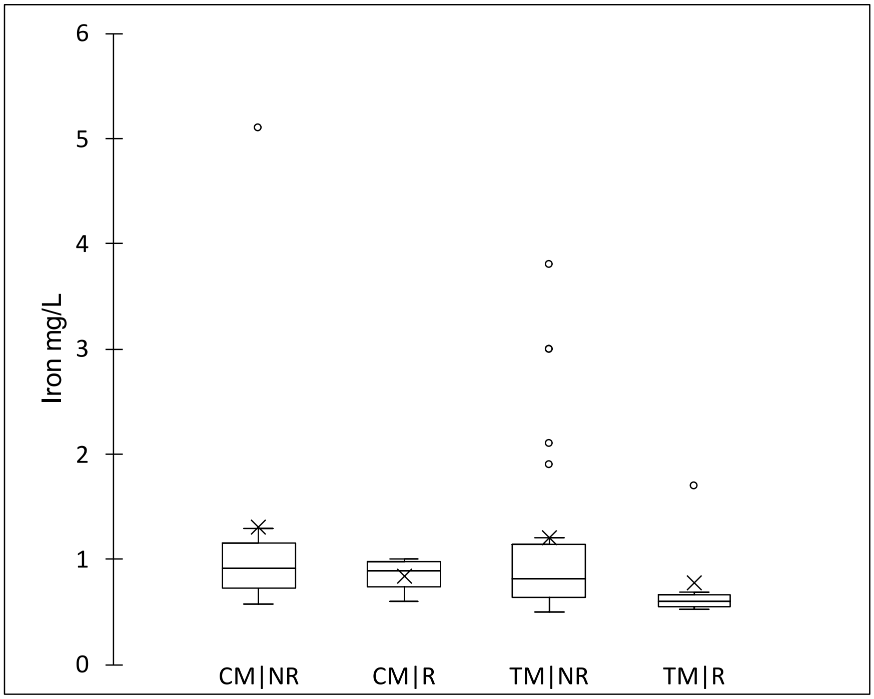

Figure S13. Box and whisker plot of Iron by production method and style for wines with measured amounts > LOD.

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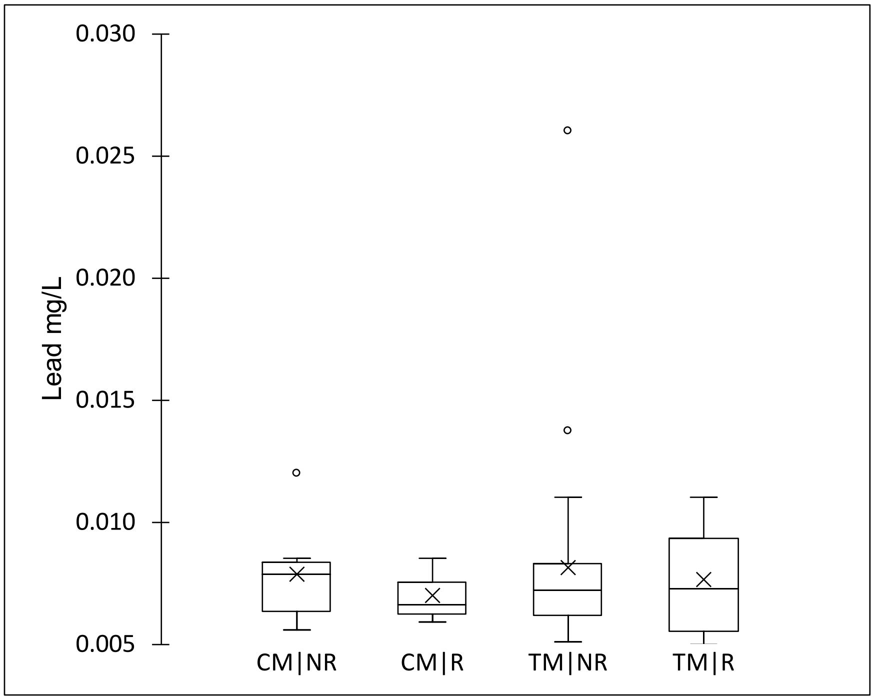

Figure S14. Box and whisker plot of Lead by production method and style for wines with measured amounts > LOD.

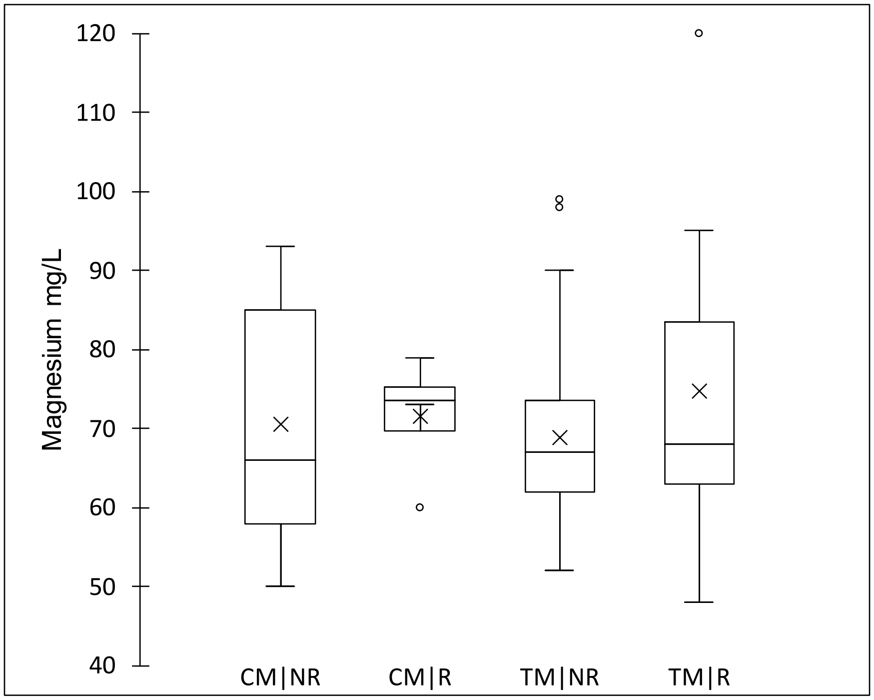

Figure S15. Box and whisker plot of Magnesium by production method and style for wines with measured amounts > LOD.

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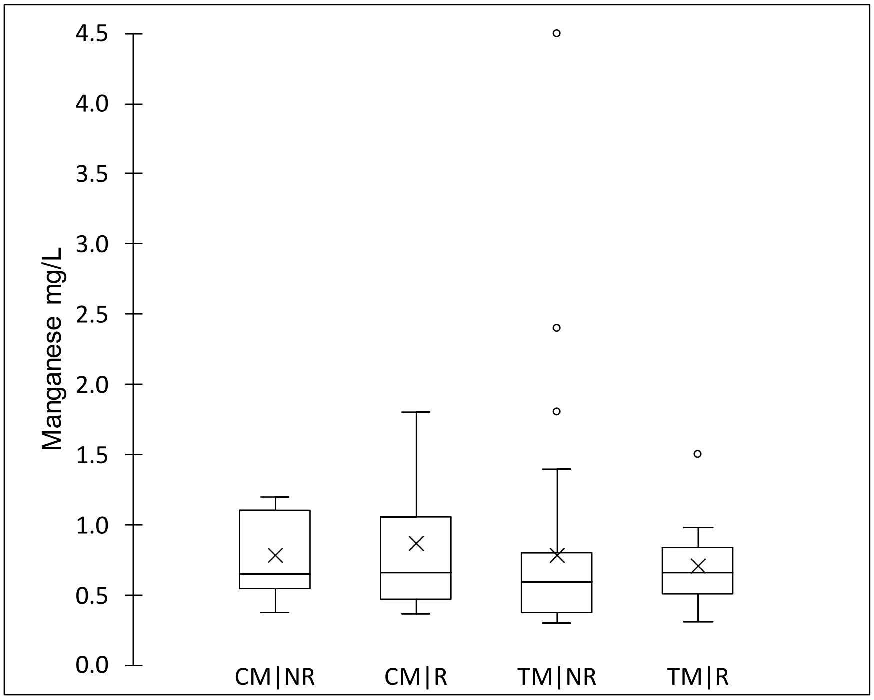

Figure S16. Box and whisker plot of Manganese by production method and style for wines with measured amounts > LOD.

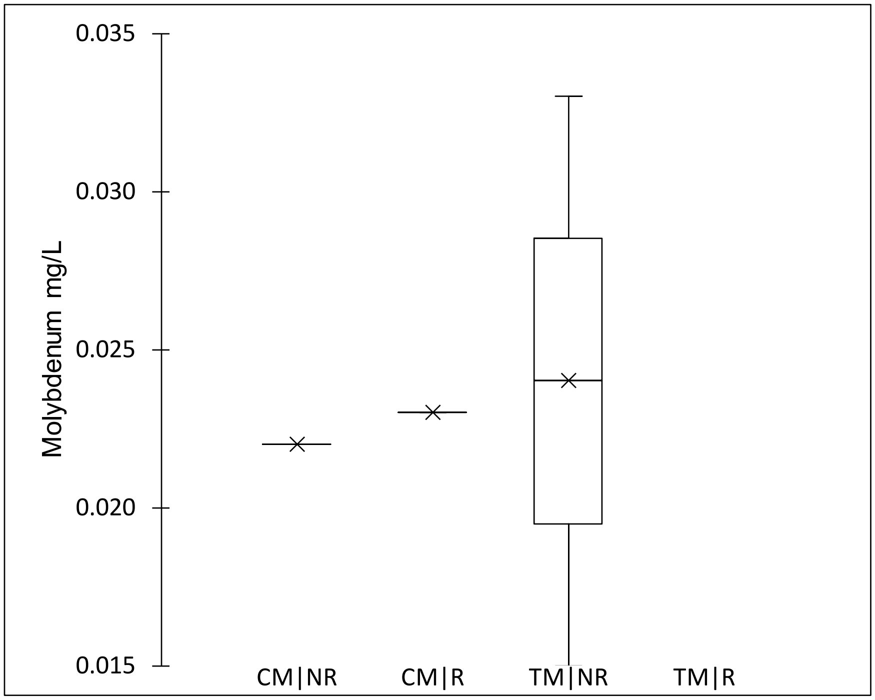

Figure S17. Box and whisker plot of Molybdenum by production method and style for wines with measured amounts > LOD.

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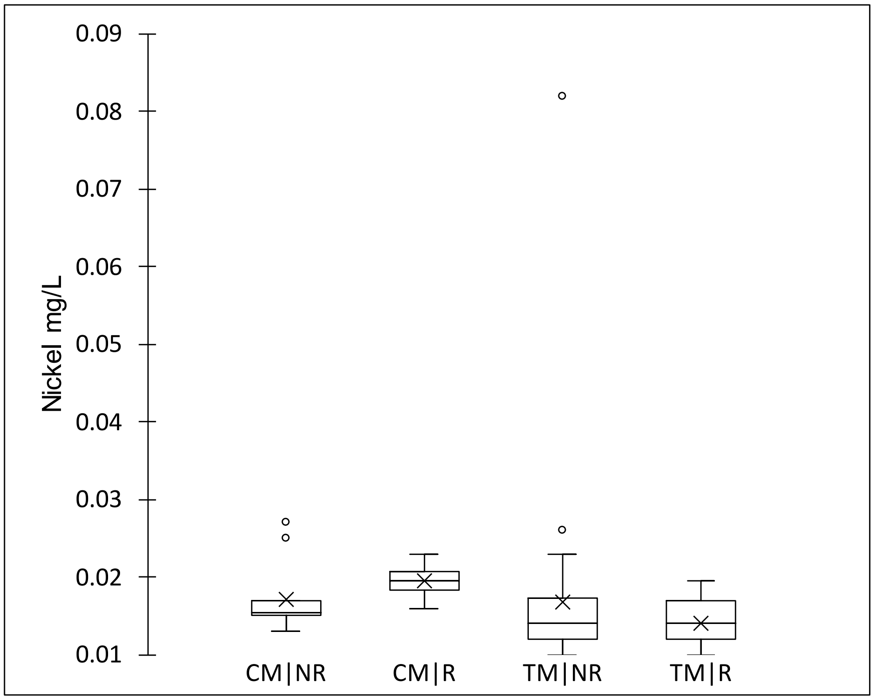

Figure S18. Box and whisker plot of Nickel by production method and style for wines with measured amounts > LOD.

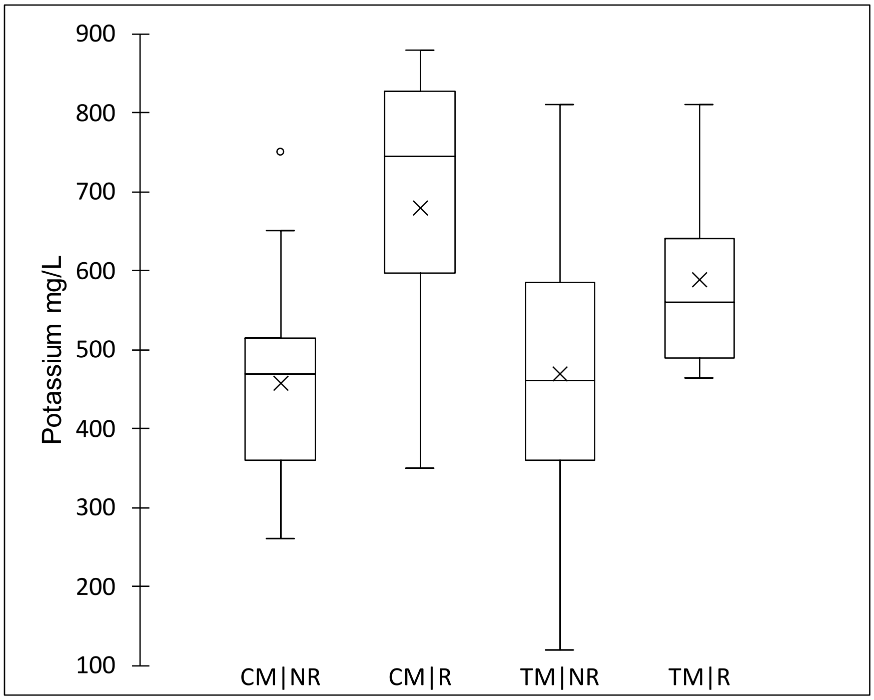

Figure S19. Box and whisker plot of Potassium by production method and style for wines with measured amounts > LOD.

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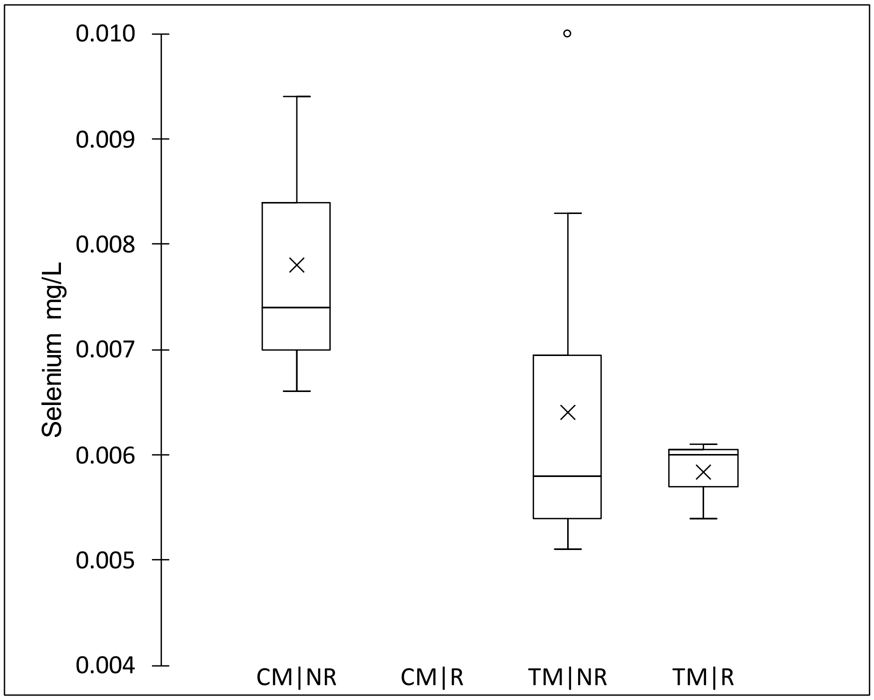

Figure S20. Box and whisker plot of Selenium by production method and style for wines with measured amounts > LOD.

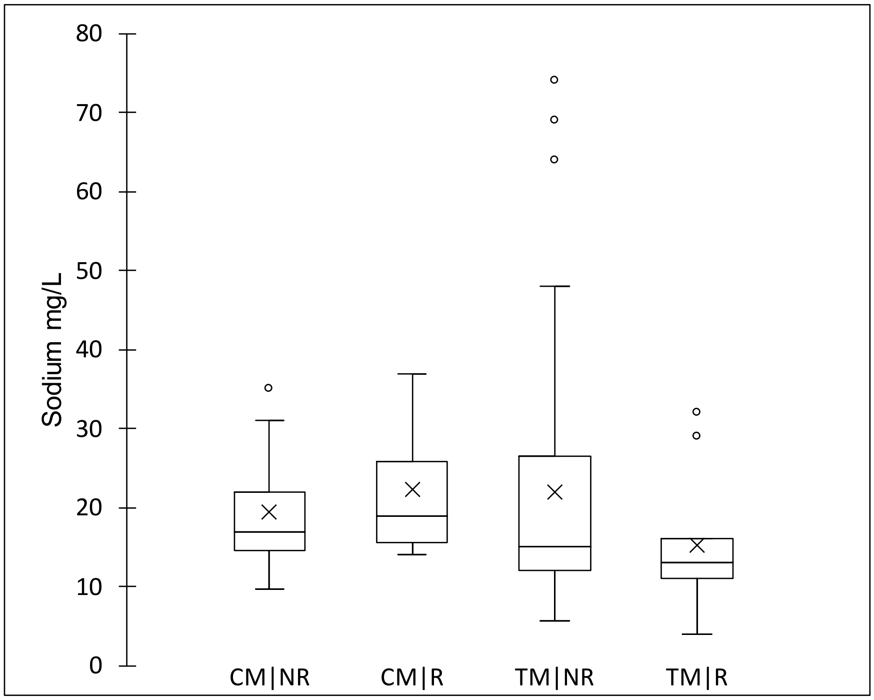

Figure S21. Box and whisker plot of Sodium by production method and style for wines with measured amounts > LOD.

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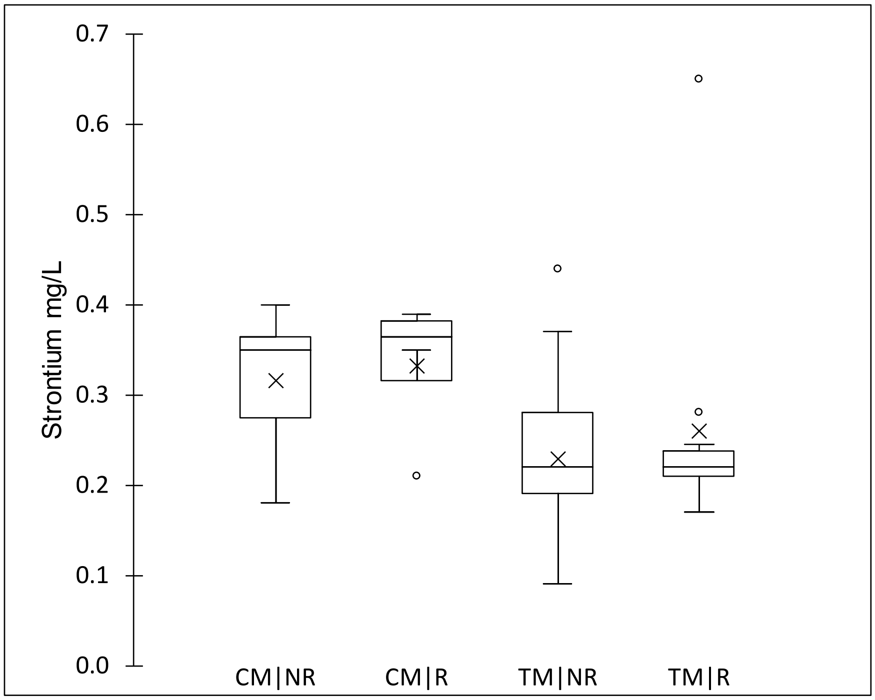

Figure S22. Box and whisker plot of Strontium by production method and style for wines with measured amounts > LOD.

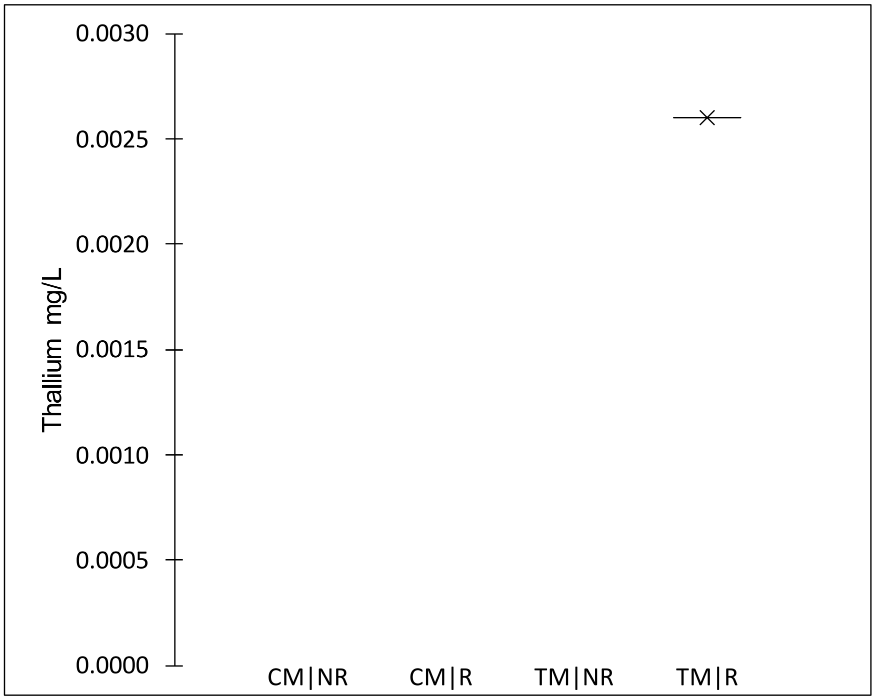

Figure S23. Box and whisker plot of Thallium by production method and style for wines with measured amounts > LOD.

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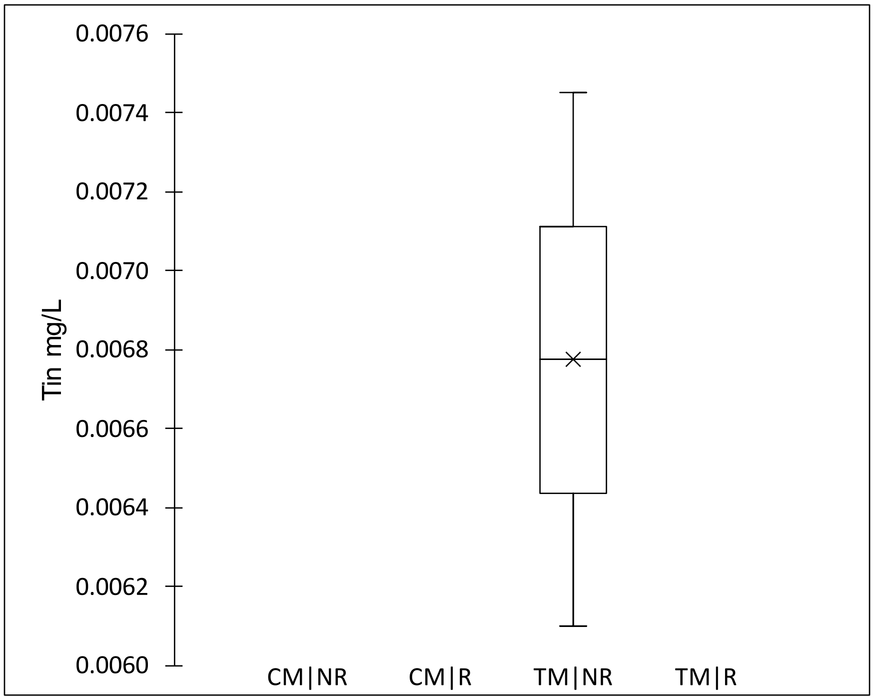

Figure S24. Box and whisker plot of Tin by production method and style for wines with measured amounts > LOD.

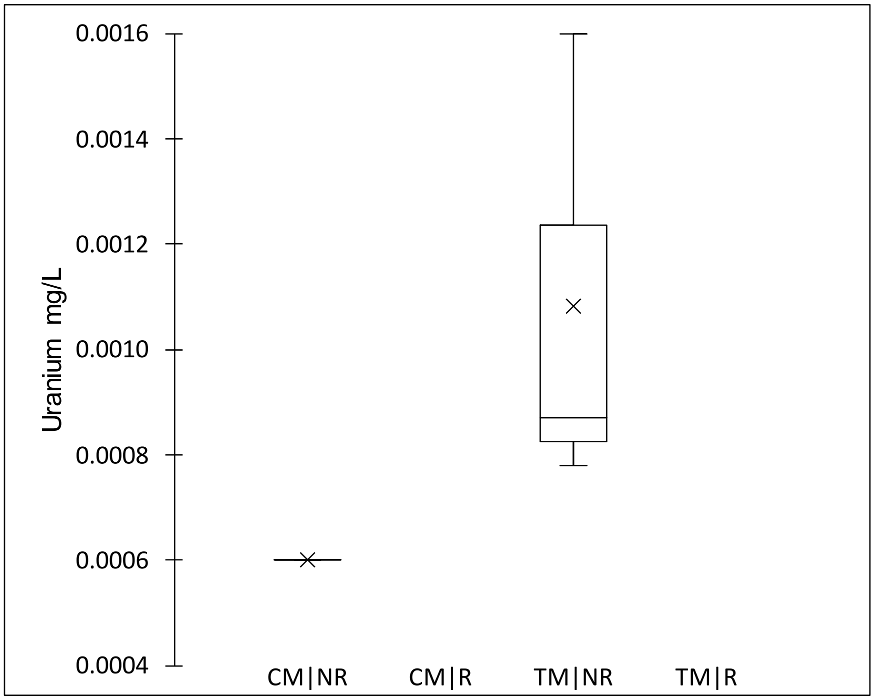

Figure S25. Box and whisker plot of Uranium by production method and style for wines with measured amounts > LOD.

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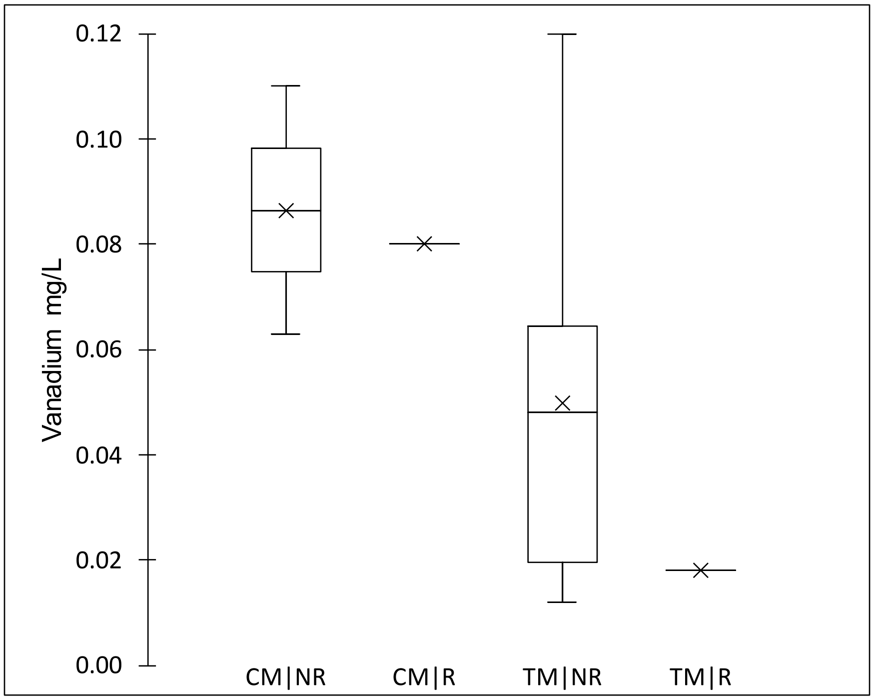

Figure S26. Box and whisker plot of Vanadium by production method and style for wines with measured amounts > LOD.

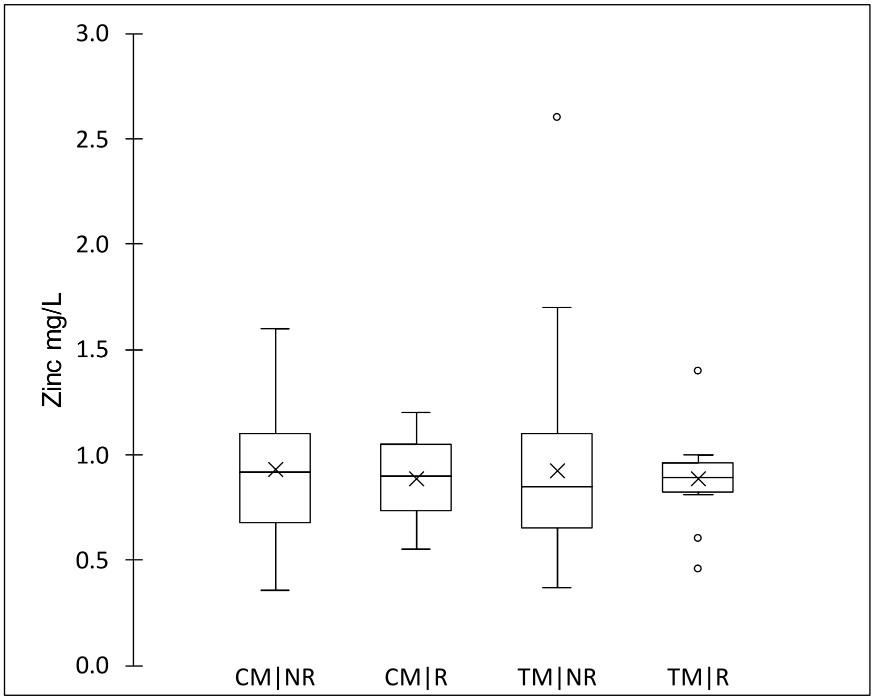

Figure S27. Box and whisker plot of Zinc by production method and style for wines with measured amounts > LOD

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(1) International Organisation of Vine and Wine (OIV). 2015. International Code of Oenological Practices - Annex: Maximum Acceptable Limits.