Production Method and Wine Style Influence Metal Profiles in Sparkling Wines

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Abstract: The elemental composition of wine provides important information about origin, authenticity, and sensory considerations. Although various wine regions and varieties of still wines have been extensively studied, limited research has evaluated the metal profiles of sparkling wines, which can be produced via the bottle-fermented traditional method (TM) or the tank-fermented Charmat method (CM) in both rosé and non-rosé styles. In this study, 73 commercial sparkling wines from Canada's Niagara Peninsula were analyzed by inductively coupled plasma-optical emission spectrometry and inductively coupled plasma-mass spectrometry to quantify 28 metal ions (silver [Ag], aluminum [Al], arsenic [As], boron [B], barium [Ba], beryllium [Be], calcium [Ca], cadmium [Cd], cobalt [Co], chromium [Cr], copper [Cu], iron [Fe], potassium [K], magnesium [Mg], manganese [Mn], molybdenum [Mo], sodium [Na], nickel [Ni], lead [Pb], antimony [Sb], selenium [Se], tin [Sn], strontium [Sr], titanium [Ti], thallium [Tl], uranium [U], vanadium [V], zinc [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 with TM wines. Cr and Ni are of particular interest because of their association with stainless steel contact during CM production. In addition, the 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 wines 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 that can inform future authenticity assessments.

Key words: elemental composition, multielemental analysis, Niagara Peninsula, sparkling wine, trace elements

The elemental composition of wine is the consequence of both natural sources and human intervention and provides important information about origin, authenticity, toxicology, sensory qualities, and nutrition (Tariba 2011, Viviers et al. 2013, Gajek et al. 2021). Specific trace elements are of particular interest due to their impact on consumer health; these include 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 Płotka-Wasylka 2021). To control metal levels in wine 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 (Supplemental Table 1) (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, and fungicides), environmental pollution, and winemaking strategies (e.g., additives, equipment, and fining agents) contribute to the type and

concentration of metal ions in juice and wine (Tariba 2011, Fabjanowicz and Płotka-Wasylka 2021, Gajek et al. 2021). Extensive research on still wines has 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 (Almeida 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 site, anthropogenic input during winemaking can introduce or modify levels of individual metals, thereby altering the metal composition during the processing of grapes from juice to wine. Total metal levels generally decrease during fermentation and aging due to their precipitation or coprecipitation with suspended solids (Almeida et al. 2003). Furthermore, 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 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. Also, 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).

Although 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 underexamined. Sparkling wine is an expanding market that accounts for ~7% of global wine production (International Organisation of Vine and Wine 2020). The Niagara Peninsula in Canada's province of Ontario is the country's largest viticultural area, containing two regional appellations and 10 subappellations regulated and administered by the Vintners Quality Alliance of Ontario. Sparkling wine production in Ontario is increasing, as shown by a 140% increase in production volume between the 2014 and 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 metal composition in sparkling wine to wine quality, as well as its application to authenticity verification, is increasingly relevant.

Sparkling wine production involves unique processing steps that 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 process, yeast, sugar, and nutrients are added to the vessel to initiate the second fermentation, thereby producing carbon dioxide and contributing effervescence to the wine. TM wines typically have minimum legal aging requirements on lees, or *sur lies*. The average *sur lies* aging duration is 12 months, although this length varies with region and vintage or nonvintage declarations. In Ontario, TM sparkling wines with a vintage declaration require a legal minimum of 12 months aging *sur lies*, whereas nonvintage 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 (one to six weeks) and less intensive production regime. 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 the juice from the grape solids postpressing. Rosé-style wines are likely to contain elevated
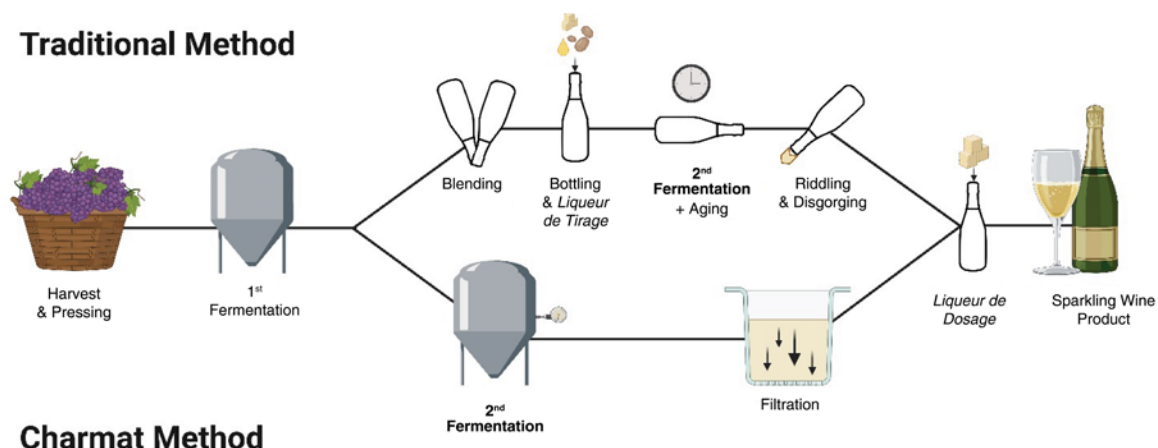
Figure 1 Overview of the production of sparkling wine via the traditional method and the Charmat method.

Table 1 Concentration ranges of metals previously identified in sparkling wines, listed by country of origin.

Concentration (mg/L)

Origin	Al[a]	As	B	Ba	Ca	Cd	Cu	Fe	K	Reference
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	(Rodrigues et al. 2020, Yamashita et al. 2019)[b]
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	(Jos et al. 2004a)[c]
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	(Jos et al. 2004a)[c]
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	(Jos et al. 2004b)[c]
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	(Rodrigues et al. 2020, Yamashita et al. 2019)[b]
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	(Rodrigues et al. 2020, Yamashita et al. 2019)[d]
Brazil	–	–	–	–	30.2–49.7	–	–	0.36–0.92	332–503	(Debastiani et al. 2021)[c]
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	(Rodrigues et al. 2020, Yamashita et al. 2019)[d]

Origin	Li	Mg	Mn	Na	Ni	P	Pb	Sr	Zn	Reference
France	0.0020–0.0230	51.8–78.9	0.39–0.65	4.0–19.2	–	–	–	0.07–0.46	–	(Rodrigues et al. 2020, Yamashita et al. 2019)[b]
France	–	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 et al. 2004a)[c]
Spain	–	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 et al. 2004a)[c]
Spain	–	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 et al. 2004b)[c]
Spain	0.010–0.023	53.9–92.6	0.48–0.82	6.2–29.1	–	–	–	0.25–1.02	–	(Rodrigues et al. 2020, Yamashita et al. 2019)[b]
Brazil	0.0018–0.0140	55.2–89.2	1.12–2.86	13.9–83.4	–	–	–	0.15–1.34	–	(Rodrigues et al. 2020, Yamashita et al. 2019)[d]
Brazil	–	42.9–62.6	1.30–1.90	10.0–18.1	–	102–131	–	–	0.62–0.90	(Debastiani et al. 2021)[c]
Argentina	0.014–0.360	56.7–147.5	0.15–1.01	27.6–344.2	–	–	–	0.38–1.29	–	(Rodrigues et al. 2020, Yamashita et al. 2019)[d]

[a]Al: aluminum, As: arsenic, B: boron, Ba: barium, Ca: calcium, Cd: cadmium, Cu: copper, Fe: iron, K: potassium, Li: lithium, Mg: magnesium, Mn: manganese, Na: sodium, Ni: nickel, P: phosphorus, Pb: lead, Sr: strontium, Zn: zinc.
[b]Only traditional-method production, with a diversity of rosé and white grape sources.
[c]Only traditional-method production, in a non-rosé (white) style.
[d]Combination of traditional and Charmat methods, with a diversity of rosé and white grape sources.

metal content compared to white sparkling wines due to 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 winegrowing regions (Greenough et al. 1997, 2005, Taylor et al. 2003, 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. 2004b). Other authors have examined metal profiles in sparkling wine to regionally discriminate sparkling wines by country of origin (Jos et al. 2004a, Yamashita et al. 2019, Rodrigues et al. 2020). Available data on the levels of metal species identified in sparkling wines are shown in Table 1. Notably, there are 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). Furthermore, to the best of our knowledge, the current literature does not compare the elemental composition of TM and CM wines or investigate 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). Evaluating wines from a single winegrowing region can provide a clear understanding of the effects of sparkling wine-making techniques on metal profiles.

Materials and Methods

Instrumentation. 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) operating in "no gas" mode and "helium kinetic energy discrimination" mode 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) due to analyte concentrations outside the linear range for the ICP-MS method (0.1 mg/L). Results were obtained with the ICP-OES instrument operating in axial mode. The wavelength used for elemental detection of B by ICP-OES was 249.678 nm.

Standard chemical analyses of wine samples were not carried out, as this study was focused solely on comparing metal composition rather than wine chemical parameters.

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 two months in the wine cellar at 14°C prior to analysis. All wines used in this study were sampled from 750-mL glass bottles. The sparkling wines included TM (43 non-rosé and 11 rosé) and CM (15 non-rosé and four rosé) wines. The higher proportion of TM and non-rosé wines approximately reflects the local industry's emerging production trends toward dry-style sparkling wines (Vintners Quality Alliance Ontario 2021). Samples were an amalgamation of wines made from a single grape variety and blends of several varieties. All analyzed wines were certified by the Vintners Quality Alliance Ontario, a regulatory body within the province intended to preserve wine quality standards and authenticity of origin. Information pertaining to geographical origin was collected from Vintners Quality Alliance label information and directly from producers. Vintages and closure types (cork or crown cap) for individual wines can be found in Supplemental Table 2.

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

Multielement ICP-MS calibration standards (Standards 1, 2A, 3, and 4) were purchased from Agilent as 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 Supplemental Table 3. For major ions including Al, calcium (Ca), Fe, potassium (K), magnesium (Mg), and sodium (Na), additional single-element 10,000 mg/L stock solutions were acquired from SCP Science and Inorganic Ventures and used to extend the calibration 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 and prepared at a 1:500 dilution (ICP-MS) and a 1:50 dilution (ICP-OES). On-line internal standards of scandium (Sc), indium (In), and bismuth (Bi) were used for ICP-MS; Sc and yttrium (Y) internal standards were employed for ICP-OES (SCP Science). Ultrapure-grade plasma gas (argon, 99.999% purity) and collision gas (helium, grade 5.0) were purchased from MEGS and Messer, respectively.

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 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), and stored at 4°C for two to three weeks until analysis. Single bottles of each wine were evaluated, consistent with previous studies that surveyed metal composition of wines (Cabrera-Vique et al. 1997, Teissedre et al. 1998, Jos et al. 2004b, Paustenbach et al. 2016, Gajek et al. 2021). All wine samples were analyzed in duplicate. Samples were degassed and diluted tenfold by diluting 2.5 mL wine to 25 mL with ultrapure deionized water. Samples (25 mL, as prepared) and quality control solutions (blanks, duplicates, and reference solutions) were measured into DigiTubes (SCP Science) with 0.25 mL concentrated trace-grade HNO_3 and 0.125 mL concentrated HCl for digestion at 90°C for 240 min. This dilution and digestion were intended to reduce matrix 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. This method of preparation, including digestion, was carried out for all method blanks, duplicates, and certified reference standards to minimize matrix effects.

Quality assurance. On-line internal standards of Sc, In, and Bi were used for ICP-MS; Sc and Y were used 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.

Statistical analysis. XLSTAT Version 2021.1.1 (Addinsoft) software was used for statistical analysis in Microsoft Excel for Mac (Version 16.47.1, 2021). 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 $p = 0.05$.

To evaluate the variability of individual metal levels by production method or wine style, multiple analysis of variance (MANOVA) was carried out for elements detected in all wine samples: B, Ca, Mg, manganese (Mn), K, Na, strontium (Sr), and 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 in which elements showed below limit of detection (LOD) values were excluded from this portion of the analysis. Due to the high proportion of nondetected (<LOD) values for many metal ions, this strategy of removing <LOD values from summary statistics therefore avoids treating <LOD values as observed measurements. Although substitution techniques (e.g., substituting <LOD values for 0, LOD, or LOD/2) have been used previously in environmental

research, they are widely considered to be outdated and inappropriate methods for handling censored data because they can skew statistics when high levels of nondetected 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 data sets were analyzed by Kruskal-Wallis nonparametric 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 in which <LOD values were eliminated from interpretation (Table 3, Figures 2 and 3).

To further evaluate relationships between metal ions and production techniques for sparkling wine, the 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, and Zn), due to the non-normal

Table 2 Parameters for inductively coupled plasma-mass spectrometry analysis of metals in wine, sorted by ion mass.

Element[a]	Ion (*m/z*)	Mode
Be	9	No gas
Na	23	He[b]
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

[a]Ag: silver, Al: aluminum, As: arsenic, 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.
[b]He: helium.

distribution of several metals in this analysis (Mg, Mn, Na, Sr, and Zn). Principal component analysis (PCA) was used to explore relationships between metal composition and production method or wine style.

Results

We analyzed the mineral compositions of 73 commercial sparkling wines produced in Canada's Niagara Peninsula. Of the 28 quantified metal ions—silver (Ag), Al, arsenic (As), B, barium (Ba), beryllium (Be), Ca, Cd, cobalt (Co), Cr, Cu, Fe, K, Mg, Mn, molybdenum (Mo), Na, Ni, Pb, antimony (Sb), selenium (Se), tin (Sn), Sr, titanium (Ti), thallium (Tl), uranium (U), vanadium (V), and Zn—Ag and Ti were not detected in any samples and were therefore removed from our results. Identified metal levels were below the internationally recommended maximum limits for wine established by the OIV. Table 3 shows the overall detected range of metals with concentrations >LOD values, as well as the values for each production method. Individual sample results are available in Supplemental Table 4, which also include box and whisker plots for each element to visualize the distribution of data for both production method and wine style (Supplemental Figures 1 to 27).

Significant differences were identified between the sparkling wine production methods. Trends toward higher mean levels of B, Cr, Ni, and Sr were detected in CM wines compared to TM wines (95% confidence interval; Figure 2). B was present in all wine samples (CM = 19 wines, TM = 54 wines). It was normally distributed (Shapiro-Wilks test) and 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 nondetected 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 the rosé wines, as were increased levels of Cu in the non-rosé wines. K was present in all wine samples (non-rosé = 58 wines, rosé = 15 wines) and normally distributed (Shapiro-Wilks test); it was thus analyzed by one-way ANOVA. However, Cu was <LOD in eight non-rosé wines (14%) and five rosé wines (33%).

The Spearman correlation matrix for metals found in all wines, namely B, Ca, Mg, Mn, K, Na, Sr, and Zn, is shown in Table 4. Low correlation ($\rho < 0.4$) relationships were shown to exist between B and 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. For TM wines (n = 54), many of the correlations in the overall data set remained consistent (Supplemental Table 5). The Spearman correlation matrix for CM wines (n = 19) shows moderate correlations

(0.4 > ρ < 0.7) between B and Na ($\rho = 0.518$; $p < 0.05$), Ca and K ($r = 0.482$; $p < 0.05$), and Mg and Sr ($\rho = 0.474$; $p < 0.05$) (Supplemental Table 6). The Spearman matrix for non-rosé sparkling wines (n = 58) revealed only weak correlations between metals, 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 ($\rho = 0.369$; $p < 0.01$) (Supplemental Table 7). For rosé sparkling wines (n = 15), 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 ($\rho = 0.554$; $p < 0.05$) (Supplemental Table 8).

PCA of the reduced data set was carried out for sparkling wines (n = 73), with the first three principal components accounting for ~60% of the variability. The biplot for principal component 1 (PC1) and principal component 2 (PC2) shows that PC1 explains ~24% of the total variance, and PC2 accounts for 19% (Figure 4). Wines were 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 were moderate positive contributors (0.5 to 0.75) to PC1, whereas B, K, and Sr provided moderate positive contributions to PC2. Few 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 ($\rho = 0.384$; $p < 0.001$). 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 no clear separation between sparkling wines when identified according to production technique (TM versus CM) or style (rosé versus non-rosé).

Discussion

Overall, the metal levels detected in our samples were comparable to those reported in the existing literature on sparkling wine (Table 1). Notably, 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 three-fold higher than the reported literature values in 48% of our Niagara sparkling wines. In comparison, mean Zn concentrations were higher than the literature values in 52% of our evaluated wines, with the maximum levels approximately four-fold higher than previously reported.

Conversely, maximum Cd concentrations in our Niagara sparkling wines were ~30-fold lower than previously reported maximum concentrations in the literature. Cd content is primarily related to fertilizer use, as prolonged or intensive application of high Cd fertilizer leads to substantial accumulation of Cd in the soil that is subsequently challenging to remediate (Reilly 1980a). 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 wine (Jos et al. 2004a). Further assessment is necessary to validate this hypothesis. In addition, elevated levels of heavy metals including Cd, As, and Pb have been linked to the use of diatomaceous earth 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 those of sparkling wines produced in the Southern hemisphere (e.g., Brazil and Argentina) than to those of European origin (e.g., France and 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, in which

Table 3 Metal concentrations with >LOD values in sparkling wines from the Niagara region produced with traditional and Charmant methods, as determined by inductively coupled plasma-mass spectrometry analysis and inductively coupled plasma-optical emission spectrometry (ICP-OES). LOD, limit of detection.

Metal[a]	Reporting limit (mg/L)	Range (mg/L)	Charmat Method (n = 19) Mean ± SD (mg/L)	Range of quantified values (mg/L)	>LOD in n wines	Traditional Method (n = 54) 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[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

[a]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, Tl: thallium, U: uranium, V: vanadium, Zn: zinc.
[b]Indicates analysis by ICP-OES (all B analyses).

individual secondary fermentation is carried out in each 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. 2004b, Paustenbach et al. 2016, Gajek et al. 2021), this source of variation warrants further research.

PCA. PCA included the metals found in all of the wines— namely B, Ca, Mg, Mn, K, Na, Sr, and Zn (Figure 4)—with samples identified according to production method (Figure 4A) and wine style (Figure 4B). Of the metal ions for which significant differences were observed between mean values for production method and wine 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 wines than in 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 the positive quadrant of PC2 appear to be strongly associated with many TM wines but no CM wines. 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 the negative quadrant of PC2 appears to be strongly associated with several CM sparkling wines but few TM wines.

The PCA biplot of sparkling wine production style (Figure 4B) shows that many rosé wines are isolated to the positive half of PC2, with two exceptions. 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 wines compared to non-rosé sparkling wines. Although our wines were collected from a relatively small geographic
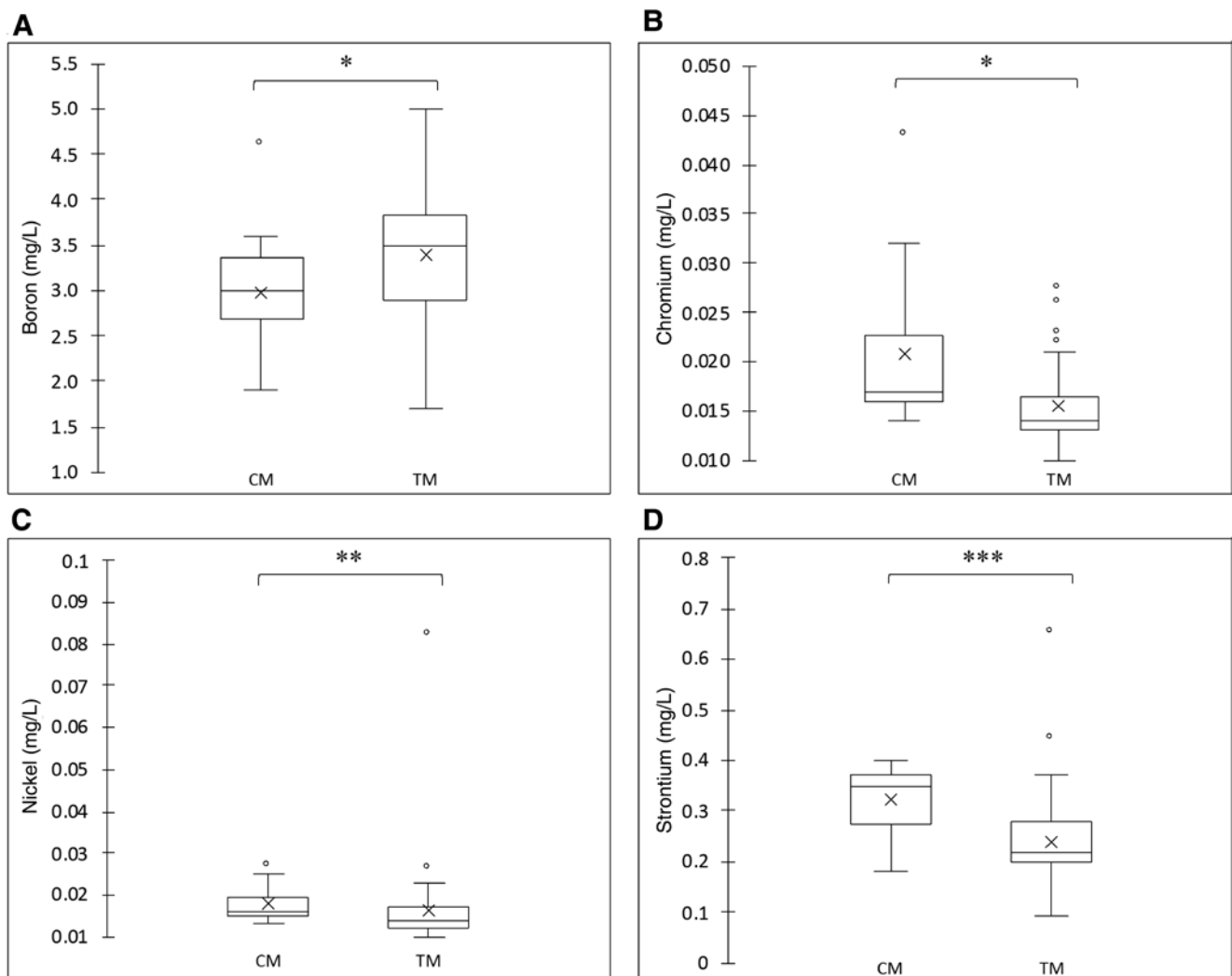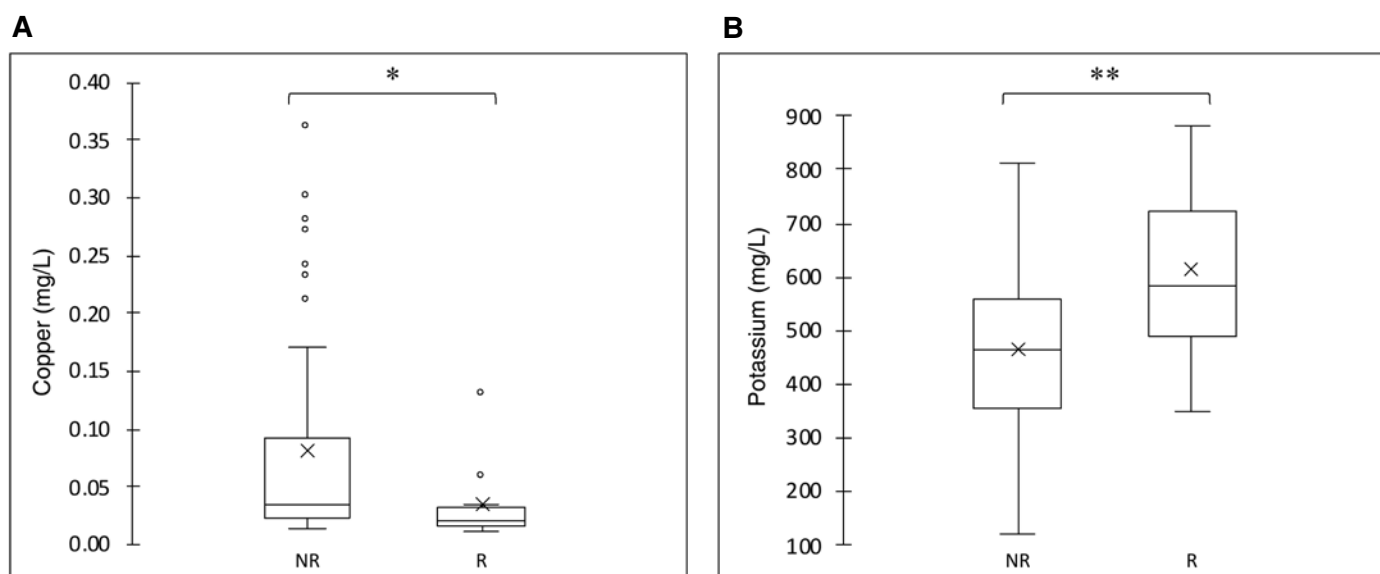

Figure 2 Box and whisker plots of statistically significant metal levels comparing the Charmat method (CM) and traditional method (TM) production techniques. (**A**) Boron, $p < 0.05$ (CM = 19 wines, TM = 54 wines); (**B**) Chromium, $p < 0.05$ (CM = 14 wines, TM = 35 wines); (**C**) Nickel, $p < 0.01$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

area of the Niagara Peninsula, elemental composition may also be affected to varying degrees by vineyard origins and the specific winemaking facility (Hopfer et al. 2015).

Elemental composition by production method. Differences in certain elemental concentrations were observed between CM and TM products. 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). Although 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

1980b). Cr is extracted into foods and beverages during manufacturing in a pH-dependent manner, with increased extraction under acidic conditions (Reilly 1980b). Due to the low pH (3.0 to 3.2) of sparkling wines, transfer of Cr from stainless steel to wine during the prolonged tank contact in CM production is possible. Furthermore, a study by Cabrera-Vique et al. (1997) demonstrated that Cr content increased with bottle age for various vintages of red wine produced by 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 leaching of chromium oxides from glass pigments in the bottle during aging. 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

Figure 3 Box and whisker plots of statistically significant metal levels 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). The area between the upper and lower edges of the boxes represents interquartile range from the 25th to 75th percentile, respectively; the internal horizontal line represents the median; and the cross indicates the mean. Whiskers above and below the boxes extend to the maximum and minimum values, respectively, with calculated outliers identified as open circular data points. Potassium was present in all wine samples but was non-normally distributed (Shapiro-Wilks test). Statistical significance for all elements was evaluated by the Kruskal-Wallis test, which indicates differences in mean rank with significance established at $p = 0.05$. Asterisks denote significant differences between groups (* or **: significant at $p < 0.05$ or 0.01, respectively).

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

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

[a]B: boron, Ca: calcium, Mg: magnesium, Mn: manganese, K: potassium, Na: sodium, Sr: strontium, Zn: zinc.
[b]*, **, or ***: significant at $p < 0.05$, 0.01, or 0.001, respectively.

fermentation vessels used in production (Skendi et al. 2020). Based on our results, higher mean levels 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 fermentation method.

Other identified elements with significant mean differences between production methods were B and Sr, which 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 amount of nutrients between the energy-intensive cycles of bloom and veraison (berry ripening) (Moyer et al. 2018). B is essential for vine growth. However, its relationship to higher content with the TM production method ($p < 0.05$) remains unclear and may instead be an artifact of the relatively small Niagara Peninsula growing region, which has ~17,000 acres of land under vine (Vintners Quality Alliance Ontario 2020).

Similarly, Sr shows no clear link to production method, and its higher levels in CM wines require further investigation. Heavy metals such as Sr have been used to authenticate wines due to their natural occurrence in soil, air, and water sources. In a multielement analysis of Canadian wines, Sr content was highly effective in discriminating between geographic origins for Canada's two major wine-producing regions, 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). Although 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. Thus, the ratio can 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 ratios of CM and TM wines may elucidate possible contaminants in the winemaking process and provide information about the relationship between Sr content in finished wine and in vineyard soil.

Elemental composition by wine style. The 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), which is presumed to be a result of maceration in rosé wine production ($p < 0.01$). 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 in white wine production (Darias-Martín et al. 2000). In red still wines, K has been identified at higher levels than in 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
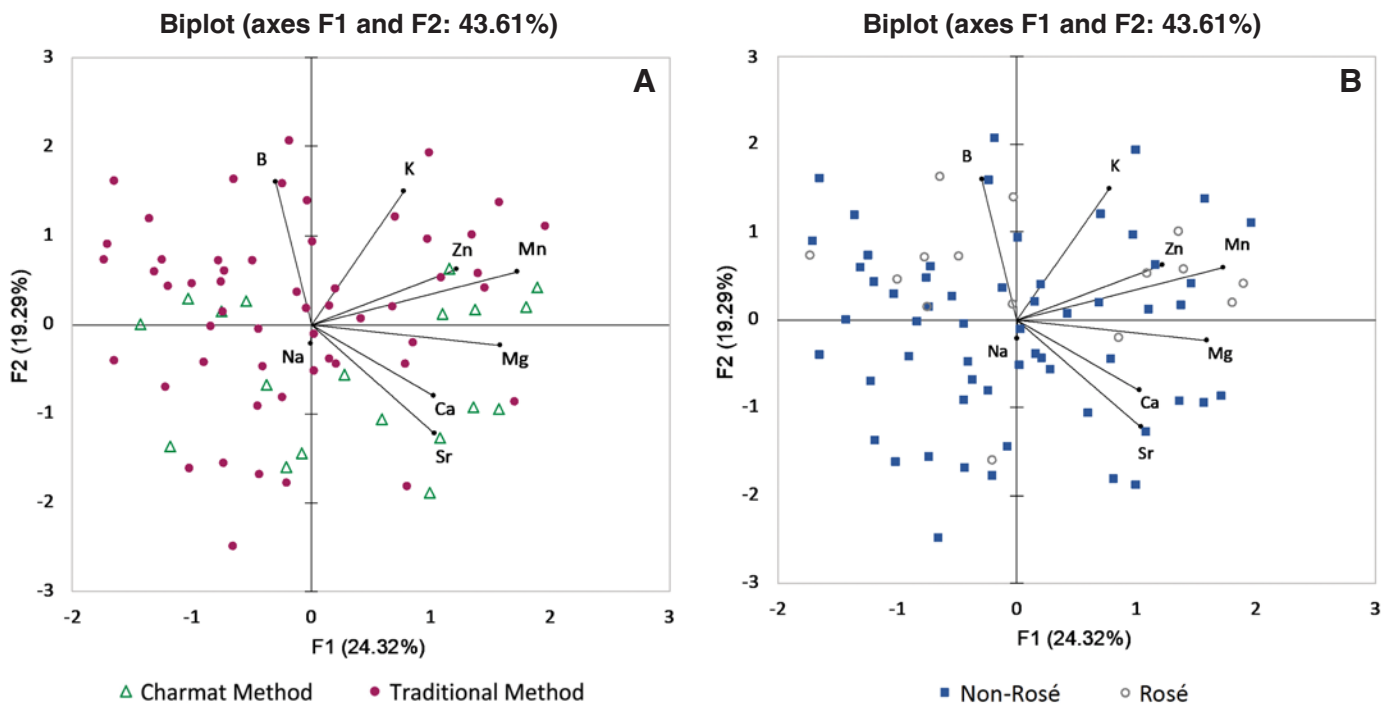
Figure 4 Principal component analysis biplot of the first two principal components for metal content of sparkling wines (only including elements with concentrations >LOD in all wines, n = 73) according to production method (**A**) and wine style (**B**). LOD, limit of detection. B: boron, Ca: calcium, K: potassium, Mg: magnesium, Mn: manganese, Na: sodium, Sr: strontium, Zn: zinc.

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 titratable acidity (g/L) levels and increased pH in wine (Ough et al. 1969, Ferreira et al. 1995).

The Spearman matrix for rosé-style wines (Supplemental Table 8) indicated 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. Notably, high K levels may also be partly attributed to nonproduction 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 and thereby impacting wine fermentation (Clark et al. 2015, Claus 2020). During fermentation, Cu is used as a yeast micronutrient, but its levels decrease substantially postfermentation, 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, which is commonly used as a treatment to remove hydrogen sulfide-related reductive off-flavors in wine (Pohl 2007, Fabjanowicz and Płotka-Wasylka 2021). The concentration of Cu has also been reported to be higher in grape skins than in pomace, but this does not explain the higher levels measured in non-rosé style sparkling wines.

Although the reason for higher Cu levels in non-rosé compared to rosé style sparkling wines remains unclear, it is notable that Cu(II) ions can catalyze the oxidation of polyphenols through the formation of reactive oxygen species, 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 the 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 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). However, 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 nonenzymatic pathways, and 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, nonenzymatic browning reactions can take place at any stage during the wine's lifetime, including during aging (Li et al. 2008).

Interestingly, in model systems, various metal ions have been shown to accelerate a specific subset of nonenzymatic browning activity called the Maillard reaction, which involves the condensation of amino acids and reducing sugars (Hyase et al. 1996, Rizzi 2008, Omari et al. 2021). Compounds associated with the Maillard reaction 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. Therefore, the role of metals in the development of desirable aroma compounds during the aging of sparkling wine remains poorly understood.

Conclusion

The results obtained in this study represent the first analysis of metals in sparkling wines produced in North America and, specifically, in Canada's Niagara Peninsula. All 73 wines contained metal concentrations within the limits set by the OIV. Moreover, levels were generally in agreement with the values previously reported in the literature on sparkling wine, although our maximum concentrations are higher than those previously reported for As and Zn. Conversely, Cd 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 wine style. Tank-fermented CM wines contained higher mean levels of Cr, Ni, and Sr compared to bottle-fermented TM wines, whereas mean B levels were higher in TM wines. Cr and Ni are components of stainless steel and are likely transferred to CM 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 they are potential candidates for use as sparkling wine authenticity markers. Compared to non-rosé sparkling wine styles, rosé wines showed higher mean K concentrations and lower Cu concentrations. Although differing K levels are likely related to the extraction of inorganic components from skins and seeds during maceration, the causes of Cu differences 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 aging of sparkling wine, as catalysts of nonenzymatic Maillard-reaction-type browning mechanisms and subsequent age-related sparkling wine flavors.

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