Effects of Frozen Materials Other Than Grapes on Red Wine Aroma Compounds. Impacts of Harvest Technologies

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Abstract: An undesirable sensory attribute ("floral taint") has been detected in red wines in North America, caused by leaves and petioles (materials other than grapes [MOG]) introduced during mechanical harvest after killing frosts. From 2017 to 2019, several harvest strategies were evaluated on Ontario Cabernet franc: hand harvest (HH), conventional machine harvesting (MECH), Braud-New Holland Opti (OPTI), Gregoire GL8, MECH + optical sorting (MECH+OS), and MECH with preharvest leaf removal (MECH+BLR). Concentrations of 41 odor-active compounds were quantified by gas chromatography-mass spectrometry. Harvest treatment effects varied by season. In 2017, HH resulted in lowest ethyl isobutyrate (MECH+BLR), ethyl nonoate, cis-linalool oxide (plus MECH and OPTI), trans-linalool oxide (plus MECH+OS), β-citral, and cis- and trans-rose oxide (plus MECH and OPTI). Ethyl hexanoate was lowest in MECH, and MECH+BLR, isoamyl hexanoate was lowest in all treatments except HH, and α-ionone was lowest in MECH and MECH+BLR. In 2018, HH resulted in the lowest β-damascenone, ethyl salicylate (plus OPTI and Gregoire), citronellol (plus Gregoire), cis- and trans-rose oxide (plus Gregoire), and eugenol (plus Gregoire). Isobutyl acetate, isoamyl hexanoate, and nerol were additionally reduced by Gregoire, and isopropylmethoxypyrazine was reduced by all treatments except HH. In 2019, harvest strategy affected 27 of 41 compounds, including 11 esters and 12 terpenes. Treatments leading to lowest concentrations were HH (nine compounds), MECH (eight compounds), MECH+BLR (10 compounds), OPTI (21 compounds), Gregoire (10 compounds), and MECH+OS (22 compounds). Wines from fruit that had undergone a killing frost contained different concentrations of 14 and eight compounds (2018), and 17 and 13 compounds (2019) for Cabernet franc and Cabernet Sauvignon, respectively. Results suggest that specific harvest technologies can reduce MOG and associated increases in aroma compounds, although seasonal differences may occur.

Key words: esters, mechanical harvest, methoxypyrazines, norisoprenoids, onoterpenes, optical sorting

Mechanized harvesting has been widely used in many grapegrowing regions for the past 50 years, but has frequently resulted in greater amounts of materials other than grapes (MOG) in harvest loads. Presence of MOG, e.g., leaves and petioles, can substantially diminish the quality and composition of wines, particularly red wines (Noble et al. 1975, Huang et al. 1988, Guerrini et al. 2018). Many studies were conducted worldwide with the advent of mechanical harvesting in the 1970s (e.g., Christensen et al. 1973, Petrucci and Siegfried 1976, Johnson 1977, Peterson 1979). Normally, mechanized harvest was considered equal to hand harvesting with respect to wine quality; however, most early mechanical harvesters were unable to expel all the MOG accumulated during harvest. Current harvesting technology has largely eliminated this problem except under unusual circumstances, such as with frost-damaged canopies (Parenti et al. 2015, Hendrickson et al. 2016). Many new mechanical harvesting technologies have optical sorting capabilities that will eject leaves, petioles, and unripe fruit (Hendrickson and Oberholster 2017, Kilmartin and Oberholster 2022). However, this equipment may not be the best financial option for grapegrowers to avoid sensory taints. Modifying vineyard management strategies such as time or method of harvest, or hand-picking specific grape varieties, may be suitable alternatives that can mitigate adverse effects of late-season mechanized harvest. This may encourage equipment companies to tailor products more toward individual grape varieties and the level of product quality, as well as the purchasing ability, anticipated by wineries. In some situations, a grapegrower with a modest acreage

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may choose custom harvesting using new equipment with sorting capabilities rather than purchasing a new harvester.

Some grape cultivars (e.g., Cabernet franc) are especially prone to a unique sensory defect, locally referred to as "floral taint," introduced by MOG following killing frosts. Warmer autumns, perhaps due to climate change, have permitted harvests of red wine cultivars such as Cabernet franc as late as mid- to late- November, when foliage had heretofore been killed by frost. It is highly likely that undesirable aroma compounds, e.g., monoterpenes and norisoprenoids, can be introduced by frozen leaves and petioles, and postfrost machine harvesting is a major contributor (Wang et al. 2020). These sensory taints, along with enabling grapegrowers to adapt to a changing climate, must both be addressed; therefore, the wine industry must understand the effects of frozen MOG on basic wine composition and wine aroma compounds, and identify harvest technologies that will minimize its incorporation into harvest loads.

Mechanical harvesting can adversely affect physical characteristics of fruit including berry damage, premature juice release, and increased MOG content (Pezzi et al. 2008, Kilmartin and Oberholster 2022). Differences in one study were largely attributed to oxidation during prolonged transport, more than differences between hand-harvested versus machine-harvested wines (Pezzi et al. 2008). Mechanical harvest results in the release of specific enzymes from both fruit and MOG, and these enzymes may come into contact with substrates (Kilmartin and Oberholster 2022). Conventional must and wine composition can consequently be adversely affected by MOG incorporation including ethanol, titratable acidity (TA), pH, malic acid, total phenol concentration, and color (Arfelli et al. 2010, Ward et al. 2015, Guerrini et al. 2018). Wine ethanol concentration can be substantially reduced with high MOG levels (Ward et al. 2015, Guerrini et al. 2018), and the presence of MOG during fermentation can additionally result in wines with higher pH and lower TA, albeit with higher malic acid concentrations (Arfelli et al. 2010, Ward et al. 2015, Guerrini et al. 2018). Incorporation of MOG into the must also has an adverse effect on color and phenolic concentration of red winegrape varieties (Wagener 1980, Huang et al. 1988, Guerrini et al. 2018). Phenolic compounds, e.g., flavanoids and tannins, can transfer from MOG into fermenting wines (Spranger et al. 2004, Suriano et al. 2016). MOG, especially petioles that are incorporated into fermentations, can also absorb anthocyanins from the fermenting must, resulting in decreased color intensity (Pascual et al. 2016, Suriano et al. 2016). However, increased MOG is frequently associated with an increase in total phenols, mainly due to elevated flavonoid concentrations in MOG-affected wines (Huang et al. 1988, Arfelli et al. 2010, Guerrini et al. 2018). High MOG levels can consequently also lead to increases in the tannin and anthocyanin concentrations in wines, and as a result, inclusion of MOG has an adverse effect on the hue and color intensity (Wagener 1980, Huang et al. 1988, Guerrini et al. 2018), often in fact leading to increases in both color intensity and hue (Guerrini et al. 2018). These alterations in the chemical composition can potentially influence the overall wine sensory profile and quality (Noble et al. 1975, Guerrini et al. 2018).

MOG may likewise affect concentrations of wine aroma compounds (Kilmartin and Oberholster 2022). The concentration and composition of volatile compounds vary depending on grapevine organ, especially among the vegetative tissues (e.g., stems, tendrils, rachis, peduncles), in addition to the berries themselves (Matarese et al. 2014). The volatile compound composition associated with the rachis, peduncles, stems, and tendrils are composed mainly of monoterpenes such as geraniol, linalool, and β-citronellol (Matarese et al. 2014). Remaining organs including leaves are composed mostly of aliphatic C6 compounds such as hexanal; 2-hexenal; 2,4-heptadienal; 2,4-hexadienal; plus 1-octen-3-ol; which are characterized by a green odor (Matarese et al. 2014). Other volatile compounds contributed by MOG are present at lower concentrations, e.g., methyl salicylate, benzyl alcohol, benzaldehyde, 2-phenylethanol, various norisoprenoids, and eugenol (Gunata et al. 1986, Matarese et al. 2014). Harvested fruit can likewise contribute to high concentrations of C6 compounds as a result of lipoxygenase activity (Kilmartin and Oberholster 2022).

Early studies found few sensory or aroma compound differences among hand-harvested and mechanically-harvested treatments (Noble et al. 1975). No increases were reported in the concentrations of leaf volatiles, such as *trans*-3-hexenal and *cis*-3-hexenol in machine-harvested must, and no sensory differences were found between hand-harvested and machine-harvested wines (Joslin and Ough 1978). However, more recent work with Pinot noir using optical berry sorting in combination with mechanized harvest demonstrated positive effects of the mechanized harvest method as well as postharvest optical sorting (Hendrickson et al. 2016, Hendrickson and Oberholster 2017). Hand-harvested fruit that was subsequently sorted produced wines with the highest dark-fruit aroma, while mechanical harvest that included the Selectiv' process (onboard MOG removal) led to higher tropical fruit aromas (Hendrickson et al. 2016, Kilmartin and Oberholster 2022). Mechanically-harvested grapes had higher concentrations of linalool, β-myrcene, α-terpinene, and β-damascenone, presumably due to glycosidic hydrolysis triggered by berry damage during harvest (Hendrickson et al. 2016). Differences in wine composition attributable to harvest treatment were reduced by postharvest optical sorting.

Floral sensory taints, observed in Ontario's commercial red wines, have been associated with mechanically-harvested grapes, so therefore it was hypothesized that increased concentrations of undesirable aroma compounds such as monoterpenes and norisoprenoids are being introduced by frozen leaves and petioles. Despite being present in very small concentrations, terpenes can have a considerable effect on the sensory properties of grapes and wines. Floral monoterpene-based aromas are typical and desirable in white wines such as Muscat, Riesling, and Gewürztraminer (Marais 1983), however, they are atypical in red table wines (Ferreira et al. 2000). It was estimated that >5% of petioles were required to substantially alter sensory attributes, particularly increasing terpene-based floral aromas in Cabernet Sauvignon (Ward et al. 2015). It is possible that prolonged autumn seasons associated with climate change, while permitting harvests later in the season, also allow for odor-active compounds such as terpenes to develop to undesirable concentrations in mature fruit. These compounds may likewise be introduced through processes such as postfrost machine harvesting. It was also hypothesized that methoxypyrazines would be reduced because of light freezing of grapes that could occur along with late harvesting, consistent with local industry anecdotal evidence. The objectives of this study were to investigate the effect of several harvesting strategies on Cabernet franc for their ability to reduce frozen MOG that negatively affects wine composition and quality. The second objective was to specifically assess the effect of freezing itself on the concentrations of aroma compounds in Cabernet franc and Cabernet Sauvignon.

A preliminary analysis of the effect of frozen MOG has appeared (Wang et al. 2020). This work extends that study to three vintages, 2017, 2018, and 2019, with a more robust data analysis.

Materials and Methods

Harvesting treatments. All Cabernet franc (*Vitis vinifera* L.) grapes were harvested following a hard frost in the 2017 to 2019 seasons from the Andrew Peller Ltd. Carlton St. vineyards, located in the Niagara Peninsula Vintners Quality Alliance (VQA) subappellation of Four Mile Creek in Niagara-On-The-Lake, Ontario, Canada. Entire rows (≈750 kg of fruit) were designated for each treatment. Treatments were hand harvest (HH), conventional mechanical harvest (MECH), MECH preceded by full canopy mechanical leaf removal (MECH+BLR), Braud-New Holland 9060L MECH with Opti-Grape system (OPTI; CHN Industrial), Gregoire GL8 MECH with EasyClean Destemmer Sorter (2018, 2019 only; SDF Group), and MECH followed by in-winery optical sorting (MECH+OS; 2017, 2019 only; Selectiv' Process Vision 2, Pellenc ST). Conventional MECH and MECH+BLR were performed in 2017 with a Braud-New Holland BRAUD 9060L without the Opti-Grape system implemented; in 2018 and 2019, MECH was performed with a Gregoire GL8 without the EasyClean Destemmer Sorter option implemented. Following harvest and/or in-winery optical sorting, grapes from each treatment were divided equally into three replicates for subsequent winemaking. Harvest dates were 14 Nov 2017, 11 Nov 2018, and 13 Nov 2019.

Frost treatments. Cabernet franc and Cabernet Sauvignon grapes were harvested prior to and following a hard frost in the 2018 to 2019 seasons from the Andrew Peller Carlton St. vineyards. Entire rows (≈750 kg of fruit) were designated for each treatment. Following harvest, grapes from each treatment were divided equally into three replicates for subsequent winemaking. Pre- and postfrost harvest dates were 4 versus 13 Nov 2018, and 5 versus 16 Nov 2019 for both cultivars).

Winemaking. Following destemming, must was treated with 50 mg/L potassium metabisulfite. Fermentations were performed in triplicates of 40 kg in 46-L plastic fermentation buckets. The fermentation vessels were then placed in a 24°C fermentation chamber and allowed to warm up overnight. Juice samples were taken immediately prior to inoculation and frozen at -25°C for future analysis. Fermentations were inoculated with 350 mg/L of yeast strain CSM (Lallemand) one day after harvest. An addition of 200 mg/L diammonium phosphate was made 24 hrs after inoculation. Fermentations were hand plunged twice daily, and fermentation kinetics (sugar concentration and temperature) were monitored daily. Seven days after destemming, the must was pressed and the wine was inoculated with the malolactic bacteria strain LACTOENOS SB3 Direct (Laffort).

Conventional analysis. Conventional chemical analysis (e.g., ethanol, TA, pH, total anthocyanins, total phenols) was also performed using standard methods. Wine pH was obtained using standard methods (Reynolds and Wardle 1989). Wine TA was measured with a PC-Titrate autotitrator (Man-Tech Associates) to a pH 8.2 end point. Color intensity and hue were determined using a modified method provided by Mazza et al. (1999) and were calculated from absorbance values measured at 420 and 520 nm on an Ultrospec 2100 Pro UV-vis spectrophotometer (Biochrom Ltd.). Total anthocyanins were measured by the pH shift method (Fuleki and Francis 1968). Total phenols were determined according to the Folin-Ciocalteu micro method (Singleton and Rossi 1965, Waterhouse 2001).

Gas chromatography-mass spectrometry (GC-MS). Wines were analyzed using GC-MS with Gerstel thermal desorption technology according to previous methods (Bowen and Reynolds 2012, Moreno Luna et al. 2018). A 30-mL sample was taken from each wine treatment replicate immediately prior to bottling and was kept at 4°C in the presence of N2 inert gas until analysis. In duplicate, 100 µL of an internal standard, prepared with 10 µL of 98% 1-dodecanol (Sigma-Aldrich) in 10 mL of 100% ethyl alcohol (Commercial Alcohols, Inc.), was poured to the mark into a 10-mL volumetric flask followed by the addition of wine and then mixed. The prepared sample was transferred into a 10-mL Gerstel extraction vial followed by the addition of 10 mL of a saturated sodium chloride solution. A 10-mm stir bar (Twister, Gerstel, Inc.) coated with polydimethylsiloxane (0.5 mm film thickness) was added to the sample and stirred for 1 hr at 1000 g for extraction at room temperature. After extraction, the stir bar was removed, rinsed with Milli-Q water (Millipore) and dried out with lint free tissue, then placed in a 4-mL amber vial at 4°C until analysis during the same day. The stir bar was then inserted inside the extraction glass tube, which was thereafter placed inside the thermal desorption unit (TDU) attached to the GC-MS.

GC-MS conditions and conditioning of materials. An Agilent 6890N/5975B GC-MS equipped with a Gerstel TDU, cooled injection system, and programmable temperature vaporization was used. Columns were Agilent 19091S-433 HP-5MS 5% phenyl methylsiloxane, nominal length 30.0 m, nominal diameter 250.00 µm, nominal film thickness 0.25 µm; and J&W 122-7032 DB-WAX nominal length 30.0 m, nominal diameter 250.00 µm, nominal film thickness

0.25 µm. Instrument conditions were identical to Bowen and Reynolds (2012) and Moreno Luna et al. (2018). MS information included solvent delay: 3 min; scan acquisition method for identification compounds, low mass: 30; high mass: 400; threshold: 150; and selective ion monitoring/scan mode for quantification of aroma compounds. Stir bars used for extraction were conditioned every time before use to avoid any cross contamination. After analysis, each stir bar was kept overnight in a solution of 80:20 acetonitrile/methanol, allowed to dry, and then placed at 250°C for 2 hrs with a constant flow of nitrogen (N2) inert gas. All glass material was washed with Milli-Q water and methanol, then dried at 250°C for 1 hr.

Calibration compounds and odor activity values. Scan analysis reflected the presence of more than 100 volatile compounds in wines from both cultivars. For calibration purposes, 41 compounds were chosen for quantification (Table 1). Seven-point calibration curves were created for each compound consistent with the literature (Bowen and Reynolds 2012). Aroma standards were obtained from Acros Organics: 1-heptanol, phenylethanol, geraniol, and β-citronellol; Fluka: 2-phenylethyl acetate, linalool, terpinolene, δ-terpinene, and diethyl succinate; and Sigma-Aldrich: ethyl isobutyrate, ethyl hexanoate, ethyl heptanoate, ethyl octanoate, ethyl decanoate, isoamyl acetate, hexyl acetate, phenylethyl acetate, isoamyl alcohol, isobutyl alcohol, 1-hexanol, 1-octanol, α-terpineol, and β-damascenone.

Model wine was used for calibration curves and prepared based on Bowen and Reynolds (2012), using 12% (v/v) of pure anhydrous ethanol (Commercial Alcohols, Inc.) diluted in Milli-Q water and 5 g/L of tartaric acid. The pH of the model wine was adjusted to 3.6 with 1N sodium hydroxide. Each aroma standard was diluted first in pure anhydrous ethanol at 1000 mg/L and kept at 4°C until analysis, then diluted at different concentrations in the model wine. Calibration samples were analyzed in SIM/SCAN mode using the same conditions as described previously with the use of the same internal standard. Odor activity values (OAVs) were calculated as a ratio between each concentration obtained by calibration versus their respective threshold. Thresholds were obtained from literature (Buttery et al. 1968, 1982, 1988, Ruth 1986, Takeoka et al. 1990, Etiévant 1991, Guth 1997, Ferreira et al. 2000, Plotto et al. 2004).

These data were used to generate concentrations of aroma compounds for comparative analysis. A list of these compounds and their aroma descriptors is found in Table 1. Methoxypyrazines were quantified by GC-MS using the methods of Kotseridis et al. (2008).

Statistical analysis. All data were analyzed using XLStat (Addinsoft). Data were also subjected to analysis of variance with mean separation by Duncan's multiple range test, $p < 0.05$. All bar plot figures were prepared using the 'ggplot' function in the 'ggplot2' package in an R environment (http://www.r-project.org/).

Results and Discussion

Effect of harvest strategy. *2017 season.* In 2017, hand harvesting resulted in lowest concentrations of ethyl isobutyrate (plus MECH+BLR), ethyl nonoate, *cis*-linalool oxide (plus MECH and OPTI), *trans*-linalool oxide (plus MECH+OS), β-citral (plus MECH and OPTI), and *cis*- and *trans*-rose oxide (plus MECH, OPTI, and MECH+OS) (Figure 1 and Supplemental Table 1). Additionally, ethyl hexanoate was the lowest in MECH and MECH+BLR, isoamyl hexanoate was lowest in all treatments except HH, and α-ionone was lowest in MECH and MECH+BLR. Overall, the treatments led to the lowest concentrations as follows: HH (seven compounds), MECH (six compounds), MECH+BLR (four compounds), OPTI (five compounds), and MECH+OS (three compounds).

2018 season. In 2018, hand harvesting resulted in lowest concentrations of β-damascenone, ethyl salicylate (plus OPTI and Gregoire), citronellol (plus Gregoire), *cis*-and *trans*-rose oxide (plus Gregoire), and eugenol (as well as Gregoire) (Figure 2 and Supplemental Table 2). Additionally, isobutyl acetate, isoamyl hexanoate, and nerol were reduced by Gregoire, and isopropylmethoxypyrazine was reduced by all treatments except HH. Overall, the treatments led to the lowest concentrations as follows: HH (six compounds), MECH (one compound), MECH+BLR (one compound), OPTI (two compounds), and Gregoire (nine compounds).

2019 season. In the 2019 season, 27 of 41 compounds were affected by harvest strategy, including 11 esters, 12 terpenes, one norisoprenoid, and three miscellaneous compounds (Figure 3 and Supplemental Table 3). The treatments that led to reduced concentrations were as follows: HH (nine compounds; two esters, five terpenes, two miscellaneous compounds), MECH (eight compounds; five esters, three terpenes), MECH+BLR (10 compounds; four esters, five terpenes, α-ionone), OPTI (21 compounds; six esters, 11 terpenes, α-ionone, three miscellaneous compounds), Gregoire (10 compounds; two esters, six terpenes, two miscellaneous compounds), MECH+OS (22 compounds; seven esters, 11 terpenes, α-ionone, three miscellaneous compounds).

When OAVs (concentration/threshold) are considered, a subset of the aforementioned compounds are considered of potential importance sensorially. Aliphatic compounds included four ethyl esters (with their 2017 to 2019 maximum OAV values): ethyl isobutyrate (OAV = 9640, 2140, 4520), ethyl hexanoate (OAV = 194, 67, 307), ethyl heptanoate (OAV = 4.6, 3.4, 6.2), and ethyl octanoate (OAV = 313, 109, 225); three acetate esters: isoamyl acetate (OAV = 48, 28, 84), isobutyl acetate (OAV = 1.7, 5.0, 8.5), and hexyl acetate (OAV = 7.8, 1.6, 4.2); and five alcohols: isobutanol (OAV = 23, 6.4, 21), isoamyl alcohol (OAV = 58, 10, 91), hexanol (OAV= 1.4, 0.3, 1.8), heptanol (OAV = 2.2, 1.8, 3.4), and phenylethanol (OAV = 20, 5.8, 19) (Figures 1 to 3 and Supplemental Tables 1 to 3). Among these compounds, all esters were responsive to harvest treatments in at least one of three seasons, and four (ethyl isobutyrate, ethyl hexanoate, isoamyl acetate, isobutyl acetate) were responsive in two seasons. None of the higher alcohols were responsive to harvest treatment. Although many terpenes were responsive to harvest treatments, only two were detected at concentrations that exceeded thresholds: geraniol (OAV = 1.5, 0.5, 0.6) and *cis*-rose oxide (OAV = 2.8, 2.2, 2.6), and of these, only *cis*-rose oxide was responsive to harvest treatment. Two norisoprenoids,

Table 1 Volatile standards for quantification of aroma compounds in Ontario Cabernet franc wines, 2017 to 2019. RT, retention time.

Compound	CAS #	RT	m/z Ions	Calibration ranges (µg/L)	Odor description[a]	Odor threshold µg/L[b]
Esters						
Ethyl isobutyrate	97-62-1	9.69	116, 71, 88	1.67-10	Sweet, rubber	0.1 (1)
Ethyl hexanoate	123-66-0	18.66	88, 99, 101	66.7-400	Apple peel, fruit	5
Ethyl heptanoate	106-30-9	22.78	88, 97, 89	3.33-20	Fruit	2.2 (1)
Ethyl octanoate	106-32-1	26.80	88, 101, 73	83.3-500	Fruit, fat	2
Ethyl nonanoate	123-29-5	30.46	101, 88, 141	8.3-50	Fruity, rose, waxy, rum, wine, natural, tropical	
Ethyl decanoate	110-38-3	34.18	88, 89, 85	66.7-400	Grape	200 (2)
2-Phenylethyl acetate	103-45-7	31.69	104, 105, 103	33.3-200	Rose, honey, tobacco	250
Isoamyl acetate	123-92-2	13.82	43, 42, 44	416.7-2500	Banana	30
Isobutyl acetate	110-19-0	10.26	73, 56, 43	41.7-250	Sweet, fruity, ethereal, banana, tropical	65 (3)
Hexyl acetate	142-92-7	19.40	43, 42, 44	4.17-25	Apple, fruity, pear, sour	2 (3)
Diethyl succinate	123-25-1	28.13	101, 129, 73	333.3-2000	Wine, fruit	200000 (4)
Isoamyl hexanoate	2198-61-0	28.70	70, 99, 117	1.67-10	Fruity, banana, apple, pineapple, green	
Alcohols						
Isobutyl alcohol	78-83-1	8.68	43, 42, 41	41667-250 000	Wine solvent, bitter	40000
Isoamyl alcohol	123-51-3	11.49	41, 42, 43	8333-500 000	Whiskey, malt, burnt	30000
Phenylethanol	60-12-08	30.47	91, 92, 93	11667-70 000	Honey, spice, rose, lilac	10000
1-Hexanol	111-27-3	16.05	56, 55, 57	250-1500	Resin, flower, green	8000
1-Octanol	111-87-5	23.77	56, 55, 57	250-1500	Chemical, metal, burnt	110 (5)
1-Heptanol	111-70-6	19.86	70, 41, 56	250-1500	Chemical, green	3; 98 (6)
Terpenes						
α-Citral	141-27-5	31.25	69, 41, 84	0.58-3.5	Lemon	14 (7)
β-Citral	106-26-3	29.90	134, 94, 69	1.03-6.2	Lemon	14 (7)
β-Citronellol	106-22-9	30.21	69, 68, 70	10, 1, 0.1	Rose	100
Eugenol	97-53-0	38.12	164, 149, 131	1.67-10	Clove, honey	6 (2)
Geraniol	106-24-1	31.77	69, 68, 70	1.67-10	Rose, geranium	30
Limonene	5989-27-5	19.69	136, 93, 107	1.67-10	Citrus, mint	15
Linalool	78-70-6	24.45	71, 72, 70	1.67-10	Flower, lavender	15
cis-Linalool oxide	5989-33-3	22.75	94, 93, 111	83.3-500	Floral, wood	
trans-Linalool oxide	11063-78-8	23.49	59, 94, 111	83.3-500	Floral, wood	
Myrcene	123-35-3	17.92	136, 93, 69	1.67-10	Balsamic, must, spice	13 (8)
Nerol	106-25-2	30.65	93, 69, 41	1.67-10	Sweet	300 (9)
Nerol oxide	1786-08-9	25.62	83, 68, 152	1.67-10	Oil, flower	
Nerolidol	7212-44-4	39.74	93, 69, 107	1.67-10	Wax	
cis-Rose oxide	3033-23-6	23.42	154, 139, 69	1.19-7.12	Green, floral, rose, lychee	0.2
trans-Rose oxide	876-18-6	24.16	154, 139, 69	0.48-2.88	Floral	450
α-Terpineol	98-55-5	28.82	59, 60, 61	1.67-10	Oil, anise, mint	330 (1)
Terpinolene	586-62-9	22.32	93, 136, 121	1.67-10	Pine, plastic	200 (8)
γ-Terpinene	99-85-4	21.01	136, 93, 121	1.67-10	Oily, woody, terpene, lemon/lime, tropical, herbal	3260 (10)
Norisoprenoids						
β-Damascenone	23726-93-4	35.25	69, 121, 190	1.67-10	Apple, rose, honey	0.05
α-Ionone	127-41-3	36.63	121, 93, 136	1.67-10	Wood, violet	0.09
β-Ionone	79-77-6	38.74	177, 135, 91	1.67-10	Seaweed, violet, flower, raspberry	2.6
Others						
Methyl salicylate	119-36-8	29.94	152, 120, 92	1.67-10	Peppermint	622 (6)
Ethyl salicylate	118-61-6	32.15	166, 120, 92	1.67-10	Wintergreen, mint	

[a] Odor description from Flavornet database (www.flavornet.org) and The Good Scents Company Information System (www.thegoodscentscompany.com).

[b] Odor thresholds obtained from Guth (1997) determined in water/ethanol (90+10, w/w). Others from: (1) Takeoka et al. 1990; (2) Ferreira et al. (2000) determined in synthetic wine 11% v/v ethanol, 7 g/L glycerol, 5 g/L tartaric acid, and pH adjusted to 3.4; (3) Buttery et al. 1982; (4) Etiévant (1991) determined in 12% water/ethanol mix; (5) Buttery et al. (1988), in water; (6) Ruth 1986; (7) Ahmed et al. (1978), in water; (8) Buttery et al. (1968), in water; (9) Leffingwell and Leffingwell (1991); (10) Plotto et al. (2004), in orange juice.

β-damascenone (OAV= 433, 23, 291) and α-ionone (OAV= 9.2, 11, 19) were also responsive to harvest treatments and might therefore be assumed to play some role in floral taint.

Basic wine composition was affected to a limited degree by harvest technologies, and these strategies also varied between seasons (Supplemental Table 4). The highest pH was measured in the MECH+BLR wines (2017, 2018) and in HH (2019), whereas the lowest pH was measured in OPTI (2017, 2018) and MECH+OS (2019). Wine TA was highest in HH (2017, 2019) in addition to OPTI (2019), and lowest in MECH+BLR (2017, 2018); all remaining treatments shared highest position for TA in 2018 and lowest position in 2019. Wine color was highest in MECH+OS and lowest in MECH+BLR in 2017, but did not differ between treatments in 2018 and 2019. Anthocyanins were highest in OPTI (2017), HH (2018), and all but HH (2019), and were lowest in MECH+BLR (2017), OPTI (2018), and HH (2019). Wine phenols were highest in HH and lowest in OPTI (2018), but there were no treatment differences in the other two seasons. Ethanol was highest in MECH+BLR and lowest in OPTI (2017 only).

The high potential of grape leaves being integrated into the fermentation following mechanical harvesting poses a

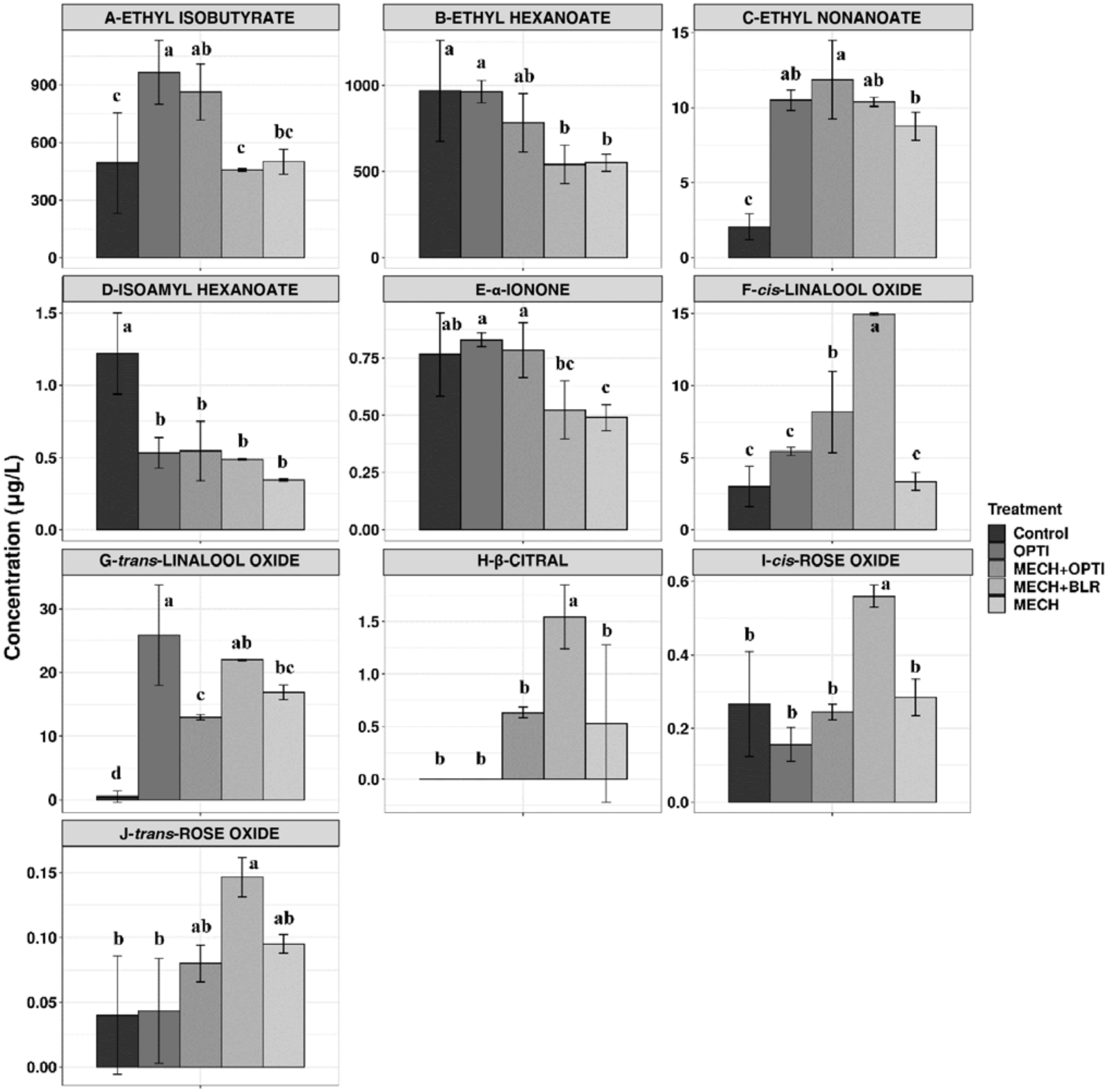

Figure 1 Effect of harvest technology on Ontario Cabernet franc aroma compounds, 2017. Control, hand harvested; OPTI, mechanically harvested using a Braud-New Holland optical sorting harvester; MECH+OPTI, conventional mechanical harvest followed by optical sorting; MECH+BLR, conventional mechanical harvest preceded by mechanical leaf removal; MECH, conventional mechanical harvest. Adapted with permission from Wang et al. (2020). Bars denoted by different letters are significantly different at $p < 0.05$, Duncan's multiple range test.

particular risk to the final wine composition (Noble et al. 1975, Wildenradt et al. 1975, Ward et al. 2015). Leaf blades (laminae) contain several volatile compounds that could potentially be extracted into wine, primarily C6 aldehydes and alcohols (2-hexanal; 2-hexen-1-ol; n-hexanol; 2-hexenol-1-ol; and hexa-2,4-dienal), terpenes (linalool, geraniol, citral, nerol, citronellol, α-terpineol, and myrcene), and norisoprenoids (β-damascenone, α-, and β-ionone) (Wildenradt et al. 1975, Gunata et al. 1986, Wang et al. 2020), although as shown in this study, many of these compounds are not necessarily detected at concentrations that exceed sensory threshold. The C6 compounds responsible for the "grassy" characteristics associated with grape leaves likely originate from lipoxygenase activity on the fatty acids in leaf cellular structures (Wildenradt et al. 1975). Petioles have high concentrations of monoterpenes, especially citronellol and geraniol (Gunata et al. 1986). The petiole may act as a storage instrument for free terpenes prior to transportation to other parts of the vine, or for utilization in metabolic pathways such as the mevalonate pathway, hence the high concentrations of terpenes in petioles compared to the laminae (Gunata et al. 1986).

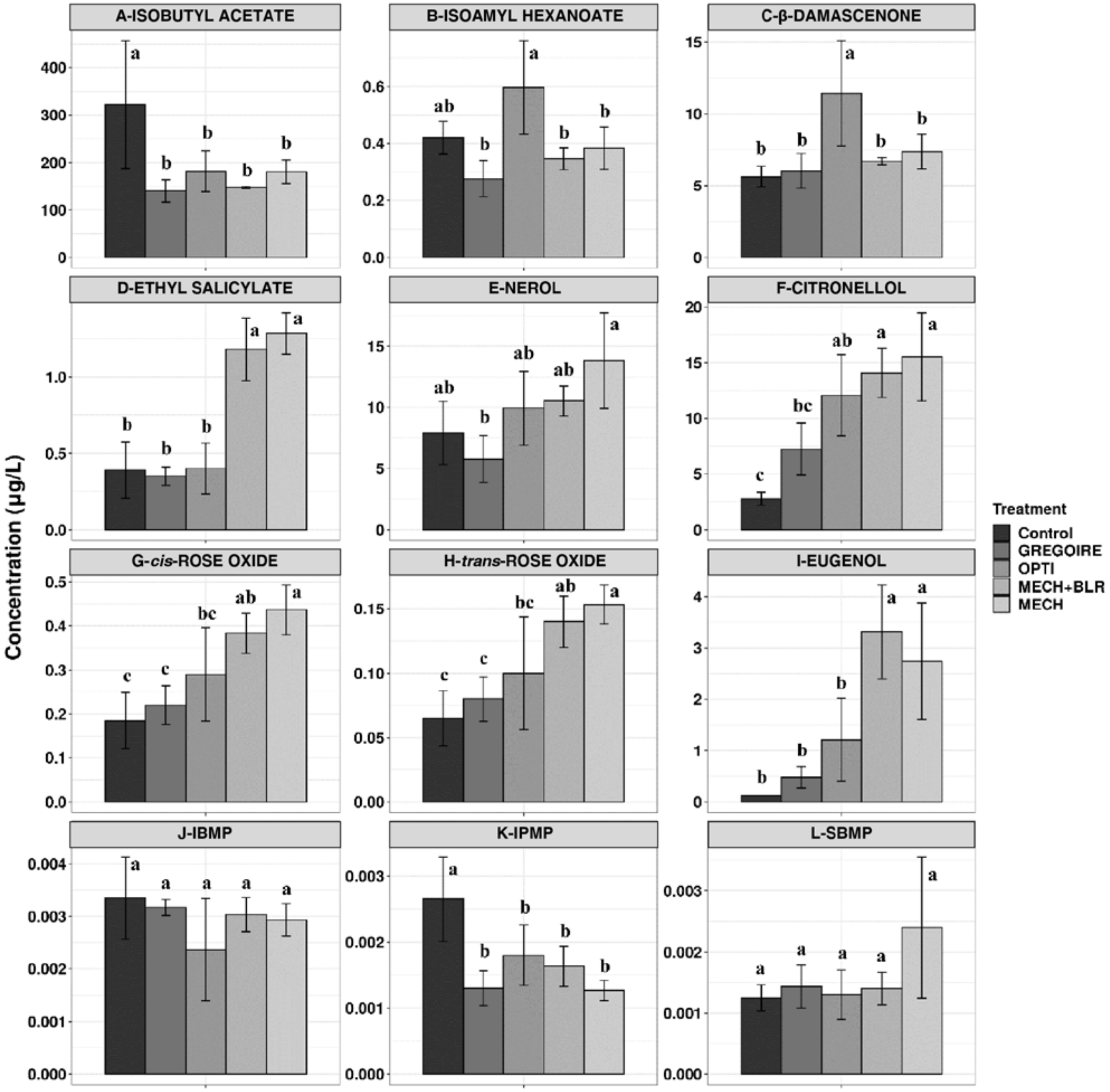

Figure 2 Effect of harvest technology on Ontario Cabernet franc aroma compounds, 2018. Control, hand harvested; Gregoire, mechanically harvested by a Gregoire GL8 harvester with optical sorting; OPTI, mechanically harvested using a Braud-New Holland optical sorting harvester; MECH+BLR, conventional mechanical harvest preceded by mechanical leaf removal; MECH, conventional mechanical harvest; IBMP, isobutyl methoxypyrazine; IPMP, isopropyl methoxypyrazine; SBPM, sec-butyl methoxypyrazine. Bars denoted by different letters are significantly different at $p < 0.05$, Duncan's multiple range test.

Juice contact with MOG during fermentation results in extraction of several volatile grapevine compounds into the final wine (Ward et al. 2015, Suriano et al. 2016, Guerrini et al. 2018, Wang et al. 2020). The presence of increasing MOG during fermentation leads to wine with higher concentrations of several monoterpenes, including geraniol, linalool, nerol, β-citronellol, and α-terpineol, as well as other aroma compounds (Ward et al. 2015, Suriano et al. 2016, Guerrini et al. 2018, Wang et al. 2020). In the presence of high MOG concentrations, geraniol, linalool, and β-citronellol may be found at concentrations above their sensory detection thresholds, suggesting a potential effect on the perceived sensory profile (Ward et al. 2015). However, only two terpenes (geraniol and *cis*-rose-oxide) were found at OAV values >1 in this study. Higher alcohols and esters increase in the presence of stems (Suriano et al. 2016, Guerrini et al. 2018). Benzyl alcohol, eugenol, 1-hexanol, methyl salicylate, and ethyl salicylate can also increase as a result of MOG incorporation (Ward et al. 2015, Guerrini et al. 2018). However, contrary to other aroma compounds found in MOG treatments, methoxypyrazines can be reduced in the presence of high petiole concentrations (Ward et al. 2015). Ward et al. (2015) hypothesized

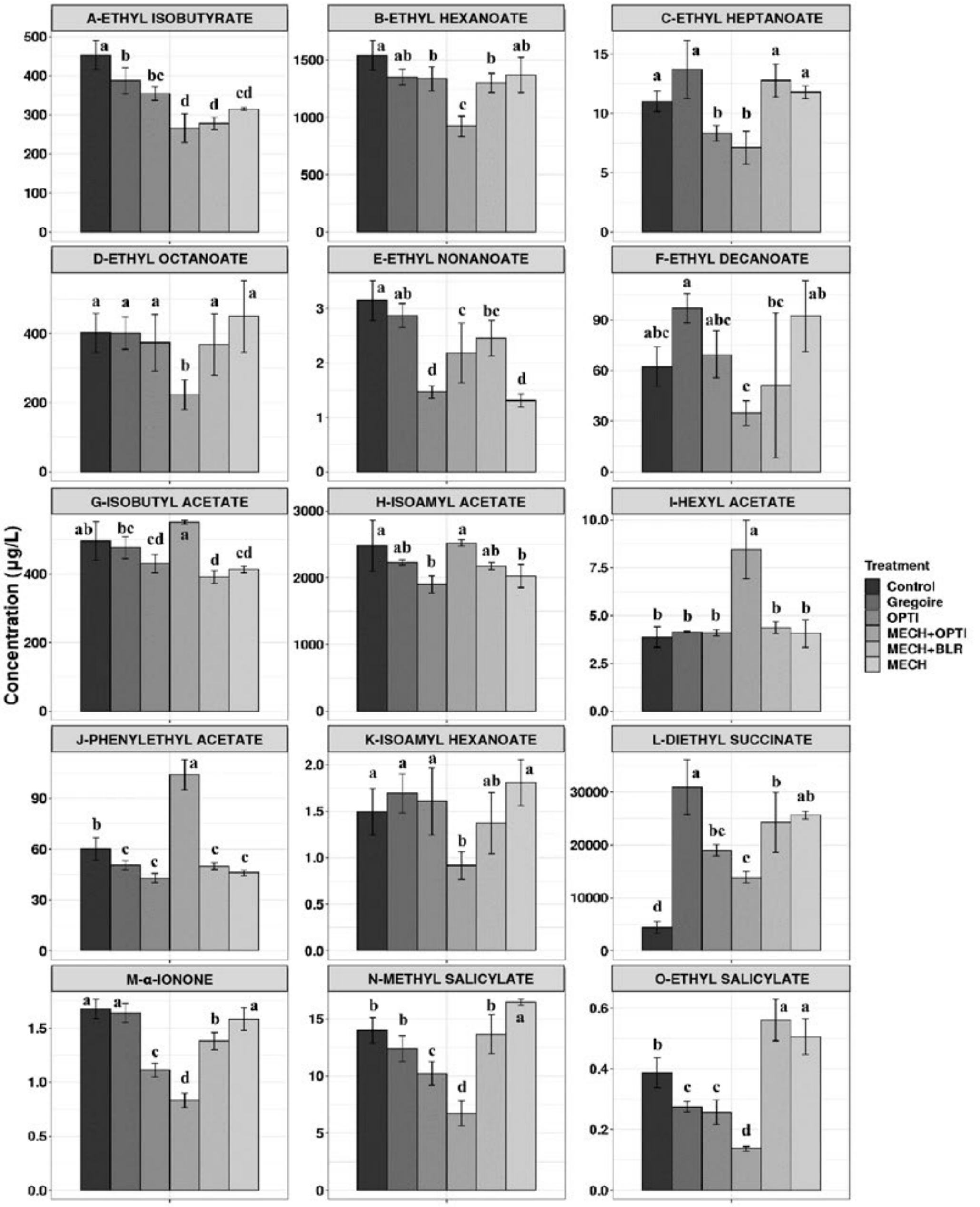

Figure 3 Effect of harvest technology on Ontario Cabernet franc aroma compounds, 2019. Control, hand harvested; Gregoire, mechanically harvested by a Gregoire GL8 harvester with optical sorting; OPTI, mechanically harvested using a Braud-New Holland optical sorting harvester; MECH+OPTI, conventional mechanical harvest followed by optical sorting; MECH+BLR, conventional mechanical harvest preceded by mechanical leaf removal; MECH, conventional mechanical harvest. Bars denoted by different letters are significantly different at $p < 0.05$, Duncan's multiple range test.

that petioles may act to adsorb 3-isobutyl-2-methoxypyrazine from the fermenting wine.

It is noteworthy that very few studies have focused on the effects of mechanical harvesters with optical sorting capabilities, or optical sorting in general, and none have addressed the effects of incorporating frozen MOG into harvest loads on ultimate wine quality. Mechanical harvesting has been documented as affecting concentrations of numerous wine aroma compounds. Esters, including isoamyl acetate and hexyl acetate, were increased in mechanically harvested Montuni grapes (Arfelli et al. 2010). Several esters (ethyl 2-methylbutyrate, ethyl acetate, ethyl hexanoate, ethyl octanoate, isoamyl acetate) differed between harvest treatments in Pinot noir in California (Hendrickson et al. 2016), although as with this study, these compounds were not the main drivers of differences between hand harvest, mechanical harvest, and optical sorting treatment combinations. Higher alcohols have likewise been affected, including increases in hexanol and butanediol, plus reductions in isoamyl alcohol and phenylethyl alcohol (Arfelli et al. 2010). As with esters, Hendrickson et al. (2016) reported differences in several alcohols (benzyl alcohol, *cis*-2-hexen-1-ol, *cis*-3-hexen-1-ol, *trans*-2-hexen-1- ol, and *trans*-3-hexen-1-ol) between harvest treatments, but again as with the current study, none were the main foundations of

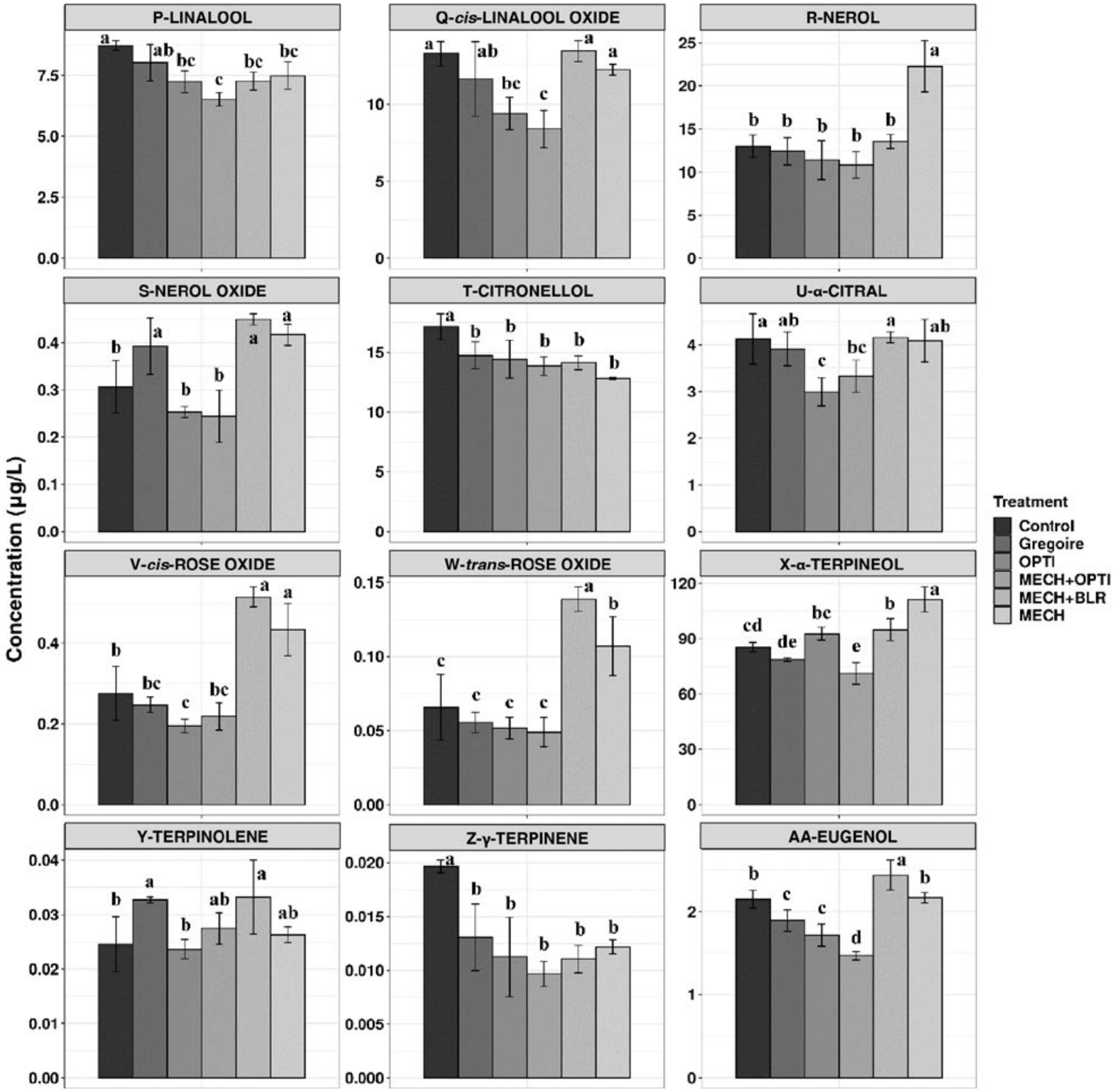

Figure 3 *continued* Effect of harvest technology on Ontario Cabernet franc aroma compounds, 2019. Control, hand harvested; Gregoire, mechanically harvested by a Gregoire GL8 harvester with optical sorting; OPTI, mechanically harvested using a Braud-New Holland optical sorting harvester; MECH+OPTI, conventional mechanical harvest followed by optical sorting; MECH+BLR, conventional mechanical harvest preceded by mechanical leaf removal; MECH, conventional mechanical harvest. Bars denoted by different letters are significantly different at $p < 0.05$, Duncan's multiple range test.

Table 2 Effect of preharvest frost on wine composition of Ontario Cabernet franc and Cabernet Sauvignon, 2018. Values are in µg/L unless otherwise specified. tr, trace.

	Cabernet franc			**Cabernet Sauvignon**		
Compound	**Before frost**	**After frost**	***p* value**	**Before frost**	**After frost**	***p* value**
Alcohols						
Isobutanol (mg/L)	108.903	256.550	**0.036** *[a]	167.863	167.187	0.985 ns
Isoamyl alcohol (mg/L)	103.100	304.365	**0.012** *	184.770	173.417	0.744 ns
Hexanol	717.133	1793.975	**0.038** *	1674.037	1594.297	0.786 ns
Heptanol	99.110	168.415	0.086 ns	216.490	186.237	0.303 ns
Octanol	23.690	36.580	0.141 ns	51.777	42.360	0.210 ns
Phenylethyl alcohol (mg/L)	24.076	53.730	**0.016** *	46.053	37.750	0.283 ns
Esters						
Ethyl isobutyrate	173.900	161.800	0.729 ns	243.853	167.833	**0.010** **
Ethyl hexanoate	68.140	282.880	**0.017** *	149.940	129.327	0.208 ns
Ethyl heptanoate	3.717	7.235	0.084 ns	7.410	5.393	**0.004** **
Ethyl octanoate	67.140	187.675	**0.033** *	138.723	114.953	0.158 ns
Ethyl nonanoate	1.583	2.045	0.397 ns	2.827	2.517	0.132 ns
Ethyl decanoate	16.773	42.660	0.061 ns	32.980	28.197	0.267 ns
Isobutyl acetate	125.313	322.670	0.070 ns	181.830	155.437	0.123 ns
Isoamyl acetate	222.060	802.945	**0.023** *	376.093	315.867	0.081 ns
Hexyl acetate	1.040	2.510	0.086 ns	2.300	1.933	0.183 ns
Phenylethyl acetate	18.247	42.975	0.055 ns	30.667	24.093	**0.041** *
Isoamyl hexanoate	0.050	0.420	**0.001** **	0.117	0.107	0.664 ns
Terpenes						
Linalool	0.293	1.055	**0.003** **	0.890	0.640	0.107 ns
cis-Linalool oxide	0.367	1.465	0.066 ns	0.727	0.507	0.139 ns
trans-Linalool oxide	0.223	0.410	0.294 ns	4.100	3.340	0.152 ns
Geraniol	1.797	14.935	**0.009** **	4.407	4.483	0.941 ns
Nerol	2.687	7.915	**0.032** *	6.230	4.783	0.114 ns
Nerol oxide	0.123	0.220	0.162 ns	0.180	0.167	0.587 ns
Nerolidol	0.117	0.245	0.216 ns	0.000	0.090	**0.004** **
α-Citral	2.517	1.930	0.202 ns	5.777	4.710	0.109 ns
β-Citral	1.710	3.625	0.080 ns	1.370	1.723	0.494 ns
Citronellol	2.980	2.780	0.697 ns	7.760	5.053	**0.049** *
cis-Rose oxide	0.163	0.185	0.576 ns	0.190	0.223	0.279 ns
trans-Rose oxide	0.067	0.065	0.898 ns	0.067	0.083	0.089 ns
α-Terpineol	5.527	19.925	0.062 ns	14.397	12.510	0.121 ns
γ-Terpinene	tr	0.010	0.272 ns	0.010	0.007	0.374 ns
Terpinolene	0.010	0.015	0.272 ns	tr	tr	-
Limonene	0.043	0.085	0.213 ns	0.143	0.073	**0.049** *
Myrcene	0.287	2.520	**0.014** *	0.583	0.753	0.633 ns
Eugenol	0.080	0.125	0.111 ns	0.347	0.093	0.081 ns
Norisoprenoids						
β-Damascenone	1.353	5.640	**0.002** **	2.943	2.617	0.315 ns
α-Ionone	0.550	0.675	0.422 ns	2.147	1.307	**0.009** **
β-Ionone	0.277	0.305	0.682 ns	0.720	0.440	**0.001** ***
Miscellaneous compounds						
Diethyl succinate	6497.233	6757.910	0.940 ns	7360.297	5689.227	0.366 ns
Methyl salicylate	2.730	2.470	0.581 ns	0.813	0.843	0.676 ns
Ethyl salicylate	0.247	0.390	0.240 ns	0.287	0.240	0.091 ns
Methoxypyrazines						
IPMP[b] (ng/L)	1.267	2.650	**0.047** *	1.400	2.133	0.227 ns
IBMP[b] (ng/L)	2.966	3.350	0.728 ns	1.433	1.933	0.426 ns
SBMP[b] (ng/L)	1.330	1.250	0.647 ns	1.700	1.100	0.457 ns

[a] *, **, ***, ns: significant at $p \leq 0.05$, 0.01, 0.001, or not significant, respectively. Significant *p* values are boldfaced.
[b] IPMP, isopropyl methoxypyrazine; IBMP, isobutyl methoxypyrazine; SBMP, *sec*-butyl methoxypyrazine.

Table 3 Effect of preharvest frost on wine composition of Ontario Cabernet franc and Cabernet Sauvignon, 2019. Values are in µg/L unless otherwise specified.

	Cabernet franc			**Cabernet Sauvignon**		
Compound	**Before frost**	**After frost**	***p* value**	**Before frost**	**After frost**	***p* value**
Alcohols						
Isobutanol (mg/L)	675.307	739.661	0.493 ns	872.434	697.073	0.157 ns
Isoamyl alcohol (mg/L)	2373.952	2742.818	0.162 ns	2840.879	2205.572	0.125 ns
Hexanol	10738.151	11168.749	0.681 ns	19793.286	22171.500	0.548 ns
Heptanol	229.036	262.875	0.166 ns	204.991	298.092	0.089 ns
Octanol	83.519	120.044	**0.022** *[a]	69.600	95.904	**0.037** *
Phenylethyl alcohol (mg/L)	131.277	147.856	0.263 ns	179.333	131.679	0.065 ns
Esters						
Ethyl isobutyrate	404.112	452.816	0.090 ns	389.828	260.855	**0.0001** ****
Ethyl hexanoate	1037.232	1538.827	**0.003** **	1086.738	1213.368	0.360 ns
Ethyl heptanoate	4.568	11.006	**<0.0001** ****	3.948	6.926	**0.008** **
Ethyl octanoate	270.231	402.494	**0.020** *	290.244	351.694	0.354 ns
Ethyl nonanoate	1.537	3.150	**0.002** **	4.258	2.770	0.088 ns
Ethyl decanoate	42.656	62.384	**0.049** *	67.887	104.788	**0.014** *
Isobutyl acetate	361.831	496.622	**0.015** *	399.261	383.161	0.478 ns
Isoamyl acetate	1649.901	2480.058	**0.021** *	1700.178	1656.169	0.493 ns
Isoamyl hexanoate	1.420	1.496	0.664 ns	1.992	1.857	0.740 ns
Hexyl acetate	3.113	3.875	0.098 ns	5.414	6.577	0.151 ns
Phenylethyl acetate	42.177	60.173	**0.009** **	50.393	49.209	0.707 ns
Terpenes						
Linalool	8.418	8.713	0.406 ns	8.915	5.642	**0.001** ***
cis-Linalool oxide	7.642	13.277	**0.001** ***	8.817	11.439	**0.002** **
trans-Linalool oxide	5.124	6.764	0.221 ns	9.809	11.453	0.410 ns
Geraniol	26.793	26.102	0.812 ns	21.761	22.133	0.828 ns
Nerol	10.149	13.007	**0.036** *	8.767	4.992	0.288 ns
Nerol oxide	0.254	0.307	0.196 ns	0.250	0.270	0.471 ns
Nerolidol	0.168	0.262	0.099 ns	0.123	0.139	0.839 ns
α-Citral	3.270	4.125	0.060 ns	3.009	3.225	0.090 ns
β-Citral	3.352	3.308	0.913 ns	1.197	0.825	0.429 ns
Citronellol	15.354	17.144	**0.048** *	11.873	13.483	**0.017** *
cis-Rose oxide	0.252	0.276	0.579 ns	0.208	0.139	**0.024** *
trans-Rose oxide	0.059	0.066	0.636 ns	0.042	0.012	**0.001** ***
α-Terpineol	36.569	85.347	**<0.0001** ****	44.361	59.336	0.052 ns
Terpinolene	0.027	0.025	0.571 ns	0.032	0.028	**0.032** *
γ-Terpinene	0.008	0.020	**<0.0001** ****	0.005	0.019	**<0.0001** ****
Limonene	0.109	0.120	0.408 ns	0.111	0.091	0.658 ns
Myrcene	1.927	3.956	0.097 ns	1.870	1.531	0.484 ns
Eugenol	1.906	2.147	**0.030** *	0.676	0.697	0.576 ns
Norisoprenoids						
β-Damascenone	10.850	14.380	**0.005** **	9.090	9.328	0.769 ns
α-Ionone	1.515	1.679	0.108 ns	2.531	2.308	0.257 ns
β-Ionone	0.369	0.418	0.074 ns	0.458	0.470	0.852 ns
Miscellaneous compounds						
Diethyl succinate	13122.899	4399.540	**0.016** *	19103.431	14840.723	0.132 ns
Methyl salicylate	16.867	13.993	0.065 ns	1.751	2.965	**0.003** **
Ethyl salicylate	0.324	0.388	0.248 ns	0.254	0.338	**0.012** *

[a] *, **, ***, ****, ns: significant at $p < 0.05$, 0.01, 0.001, 0.0001, or not significant, respectively. Significant p values are boldfaced.

treatment differences. Several organic acids have been reduced by mechanical harvesting, including isobutyric, isovaleric, and phenylacetic acids, whereas hexanoic, octanoic, and decanoic acids have been reported to increase, but their sensorial significance was not discussed (Arfelli et al. 2010).

Of greatest concern in this study were those compounds with low sensory thresholds—terpenes and norisoprenoids in particular—which were likely to be the main source of floral taint in wines produced from fruit mechanically harvested subsequent to killing frosts. In Australia, Cabernet Sauvignon wines produced from fruit with high MOG concentrations had geraniol, linalool, and β-citronellol concentrations above their detection thresholds, suggesting a potential sensory effect (Ward et al. 2015). Machine-harvested Pinot noir grapes in the Russian River Valley in California had higher concentrations of linalool, β-myrcene, α-terpinene, and β-damascenone, which were attributed to glycosidic hydrolysis due to berry damage during harvest or from wounding response-induced synthesis (Hendrickson et al. 2016). Other terpenes affected by mechanical pruning treatments included geraniol, nerol, nerol oxide, citronellol, and two sesquiterpenes (Hendrickson et al. 2016).

Impact of killing frost. Wines produced from fruit that had undergone a killing frost contained higher concentrations of 14 and eight compounds in 2018 in Cabernet franc and Cabernet Sauvignon, respectively (Table 2 and Supplemental Figure 1), and 17 and 13 compounds in 2019 in Cabernet franc and Cabernet Sauvignon, respectively (Table 3 and Supplemental Figure 2). Cabernet franc volatile compounds in most cases increased after a frost event; in 2018 these included four alcohols (isobutanol, isoamyl alcohol, hexanol, and phenylethanol), three esters (ethyl hexanoate, ethyl octanoate, and isoamyl acetate), five terpenes and norisoprenoids (linalool, geraniol, nerol, myrcene, and β-damascenone), and isopropyl methoxypyrazine (IPMP). In 2019, compounds that increased postfrost included octanol, eight esters, six terpenes (*cis*-linalool oxide, nerol, citronellol, α-terpineol, γ-terpinene, and eugenol), and β-damascenone. In Cabernet Sauvignon in 2018, only nerolidol increased after frost, whereas three esters (ethyl isobutyrate, ethyl heptanoate, and phenylethyl acetate) and four terpenes and norisoprenoids (citronellol, limonene, α-ionone, and β-ionone) decreased. In 2019, eight of 13 affected compounds increased after frost, including octanol, ethyl heptanoate, ethyl decanoate, *cis*-linalool oxide, citronellol, γ-terpinene, methyl salicylate, and ethyl salicylate. Ethyl isobutyrate, linalool, *cis*-rose oxide, *trans*-rose oxide, and terpinolene decreased. It is noteworthy that none of the methoxypyrazines were reduced by frost in either cultivar, contrary to the widespread anecdotal evidence in the Ontario industry.

The effect of frost on the ultimate basic wine composition was limited for both cultivars (Supplemental Table 5). For Cabernet franc, prefrost wines had slightly higher pH in 2018, but there were no other effects in that season and none in 2019. For Cabernet Sauvignon, there were no effects in 2018; freezing increased pH and reduced TA in 2019. No other effects were observed.

Studies into preharvest freezing of grapes intended for table wines are uncommon. Lan et al. (2016) reported that Beibinghong berries sampled in the last stages of maturity (which included freezing) were characterized by several terpenes (e.g., *cis*- and *trans*-linalool oxides and *cis*- and *trans*-rose oxides), norisoprenoids (*cis*- and *trans*-theaspirane and vitispirane A and B), and higher alcohols (e.g., heptenol, 2-octanol, and 1-butanol). In a related study involving comparisons with table wines produced from nonfrozen grapes, Beibinghong icewines made from frozen grapes were characterized by higher concentrations of volatile phenols, lactones, β-damascenone, phenylacetaldehyde, and diacetyl, versus corresponding dry wines made from fresh grapes (Lan et al. 2019). These differences were ascribed to “complex reactions induced by water loss and freezing-thawing events” during the on-vine dehydration and freezing processes. Delayed harvest of four cultivars in Ontario (Pinot gris, Riesling, Cabernet franc, and Cabernet Sauvignon), which involved brief freezing episodes for the red cultivars, resulted in substantial changes in most wine aroma compounds (Moreno Luna et al. 2018). Pinot gris and Riesling displayed increases in monoterpenes, norisoprenoids, esters, aldehydes, and alcohols in wines from late harvested fruit. Reduced concentrations of volatile acids and green odor compounds (e.g., 1-hexanol) with delayed harvest were also evident. Delayed harvest was also associated with the production of benzaldehyde, diethyl acetal, and higher concentrations of higher alcohols (e.g., isoamyl alcohol and nonanol), which could have been associated with preharvest desiccation rather than freezing. Cold maceration (without freezing) with automatic pump-over of Cabernet Sauvignon resulted in decreases in isobutanol and isopentanol and an increase in some esters (especially acetate esters) (Cai et al. 2014). Ethyl 2-hexenoate and diethyl succinate were decreased, and geranyl acetone was increased in both pump-over and punch-down fermentations, whereas β-damascenone increased by cold maceration in pump-over fermentations but decreased in punch-down fermentations.

Studies with harvest dates for icewine grapes suggest effects of multiple freezing events on aroma compounds. In an investigation of Ontario Vidal blanc and Riesling icewines, the highest concentrations for most aroma compounds were found in the latest of three harvest dates (16 of 24 for Vidal; 17 of 23 for Riesling) (Bowen and Reynolds 2015). The latest harvest date had the highest ethyl isobutyrate, ethyl 3-methylbutyrate, 1-hexanol, 1-octen-3-ol, 1-octanol, *cis*-rose oxide, nerol oxide, ethyl benzoate, ethyl phenylacetate, γ-nonalactone, and β-damascenone. The earliest harvest, which still had experienced at least one freezing episode, had the highest ethyl butyrate, ethyl hexanoate, linalool, 4-vinylguaiacol, and ethyl octanoate. However, there were no table wines produced in this study with which to compare the icewines to ascertain the effects of freezing. Similarly, Lutskova and Martirosyan (2021) compared early and later icewine harvests for four cultivars (Rkatsiteli, Telti kuruk, Marselan, and Moldova) and reported differences in aroma compounds; for example, Rkatsiteli icewine obtained from an early icewine harvest contained highest concentrations of geraniol, 1-octanol, and 2-phenyl acetate, while highest concentrations of ethyl hexanoate and ethyl octanoate were detected in the icewines from red cultivars Moldova and Marselan from a later harvest. However, once again, no wines produced from nonfrozen grapes were included for comparison.

Conclusions

These results suggest that specific harvest technologies can reduce MOG and its associated increases in undesirable aroma compounds, although seasonal differences may occur. It is apparent that mechanical harvesters with sorting capabilities can reduce MOG and consequently lower concentrations of compounds, such as terpenes, that may be associated with floral taints. In-winery optical sorting following conventional mechanical harvesting is likewise efficacious. A limited number of ethyl esters (ethyl isobutyrate, ethyl hexanoate, ethyl heptanoate, and ethyl octanoate); three acetate esters (isoamyl acetate, isobutyl acetate, and hexyl acetate); one terpene (*cis*-rose oxide), and two norisoprenoids (β-damascenone and α-ionone) were responsive to harvest treatments and also found at concentrations above sensory thresholds. Moreover, several esters, terpenes, and norisoprenoids increased following killing frost in hand-harvested grapes, suggesting that enhanced harvest technologies may not entirely overcome issues of floral taints in red wine cultivars.

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