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Understanding Smoke Taint Results: Pinot noir Baseline Concentrations of Smoke Taint Markers across Five Vintages

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Summary

Goals: With increased wildfires in recent years, winemakers now regularly need to interpret smoke taint results to determine if smoke intrusion has impacted their wines. The goal of this study was to examine naturally occurring baseline levels of smoke taint marker compounds in un-oaked Pinot noir to enable winemakers to better understand smoke taint results. This study also sought to understand how baseline concentrations of smoke marker compounds change from year to year.

Key Findings:

- Pinot noir wines from California and Oregon had detectable baseline levels of free and bound marker compounds, including guaiacol, 4-methylguaiacol, 4-ethylphenol, and, *m*-, *p*-, and *o*-cresol. In 2019, the baseline free guaiacol concentration ranged from 1.2–2.3 µg/L, while total (free and bound) guaiacol ranged from 6.4–12.0 µg/L.
- The concentration of free guaiacol was greater in older vintages, while total guaiacol largely did not change from year to year.
- The ratio of free to total guaiacol approached 1:2 after 5 years, suggesting baseline guaiacol may approach an equilibrium over time.

Impact and Significance: While baseline levels identified here were low, winemakers should become familiar with the baseline concentrations in their wines to better understand risk during smoke impacted vintages. With increased analysis of non-smoke impacted, baseline samples, it may be possible to create a risk matrix by wine variety for smoke taint exposure. Additionally, as wines age, free volatile smoke marker compounds may increase due to normal changes to baseline compounds and may not always represent smoke glycosides releasing free volatiles.

Overview

Wildfire smoke has caused concern for wine quality around the world in the last two decades. As fires burn, volatile phenols are generated from the breakdown of lignin. Depending on the wood source, different types of volatile phenols are also present in the smoke.¹ These volatile phenols are then taken up by the plant, either directly through the fruit, or through the leaves and translocated to the fruit.² Although multiple compounds are responsible for smoke aroma, guaiacol and 4-methylguaiacol are often used as key exposure markers because they are typically found in the highest quantities in smoke exposed grapes and wines.³ Other compound classes implicated in smoke taint aroma include syringyls (syringols), *p*-hydroxy-phenyls (phenols and cresols), and guaiacyls (guaiacols and eugenol).¹ Baseline concentrations of these compounds in different wine varieties need to be established to better understand risk attributed to smoke exposure during smoke impacted vintages.

When volatile phenolics are taken up by the plant, they are bound to sugar molecules to minimize the toxic effect on the plant.^{3,4} Many researchers are currently examining exactly which of these glycoconjugates form and how these compounds change over time in winemaking.^{5,6} However, due to a wide range of compounds present, this approach can be challenging for commercial laboratories to use as a screening tool for routine analysis. Acid or enzyme hydrolysis are techniques utilized to estimate the concentrations of this group of compounds by releasing them into their free volatile form.³ Because sample analysis by acid or enzyme hydrolysis measures both initially free volatiles and volatile compounds released through the hydrolysis process, the protocol estimates the total pool of smoke phenolics present in a wine. While there are drawbacks to both acid and enzyme hydrolysis, including the

formation of artifacts, acid hydrolysis has been found to be more reflective of grape and wine aroma than enzyme hydrolysis.⁷

Sensorially, free volatile phenols are primarily responsible for smoke taint aroma and taste,⁸ while glycosylated compounds contribute to smoke flavor and aftertaste.^{2,9} Bound compounds may also hydrolyze to release their free volatile form during aging of a wine, making smoke aroma worse over time.¹⁰ This temporal change in free volatile phenolics has been most significantly noted regarding mitigation efforts, such as when wines are treated with reverse osmosis filtration, but smoke aroma returns over time.¹¹ It is important to measure both free and bound compounds to assess both the immediate smoke impact as well as the potential long-term risk.

Additionally, it is important to be familiar with baseline concentrations of both free and bound compounds to properly understand risk. Free and bound guaiacol has been previously identified in non-smoked Merlot, Cabernet Sauvignon, Syrah, Tempranillo, Grenache, and Viognier.^{3,12-15} Many of the baseline concentrations currently published are from control wines in smoke taint research. For example, non-smoked Merlot wine has been shown to have 4 µg/L guaiacol, and trace levels (less than 1 µg/L) of 4-ethylguaiacol, 4-ethylphenol, and eugenol.^{1,3} While these concentrations are often many orders of magnitude lower than concentrations for smoked fruit and wines, commercial labs have found that red wines with free guaiacol concentrations over 6 µg/L lead to smoky aromas.¹³ Internal winemaking sensory panels have also anecdotally noted the presence of smoke taint at or above 4 µg/L guaiacol. With such a narrow margin between normal and potentially smoke impacted results, winemakers will be better prepared to make risk assessments if they are aware of the typical baseline concentration in their own wines.

To date, baseline concentrations of smoke volatile phenols are not widely available. Researchers at AWRI (Australian Wine Research Institute) have conducted an intensive baseline survey, but this data has not yet been published.¹⁶ Additionally, there is a limited understanding of the impact of growing conditions and site on the level of baseline concentrations. This study aims to examine baseline concentrations of common smoke taint marker compounds in Pinot noir wines from 15 different vineyard sites in California and Oregon. This study also aims to compare concentrations of these compounds in wines at various stages of aging, so that winemakers can better interpret the relative impacts on their wines at any stage of maturation. Thus, allowing for better interpretation of general risk when fires erupt in their winegrowing regions.

Major Observations and Interpretations

Pinot noir wines produced over 5 vintages (2015–2019) from California and Oregon were examined at the same time-point (February 2020) for volatile smoke compounds including guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-ethylphenol, and *m*-, *o*-, and *p*-cresol. Thirteen vineyard sites were analyzed in California and two were analyzed in Oregon (Figure 1). Over those five vintages, only one wine from 2018 was excluded due to potential environmental smoke impact. Concentrations of both free and total volatile phenolics were measured. For clarity, we will use the terminology ‘total’ to refer to the concentration after acid hydrolysis. Additionally, in this study *p*- and *m*-cresol both showed peak degradation after acid hydrolysis and were therefore only included in the free volatile data analysis.

Pinot noir wines from various regions in California and the Willamette Valley of Oregon had detectable baseline levels of all measured smoke volatile phenols, except 4-ethylguaiacol

(Table 1). The concentration of all free volatile phenols was relatively low. In wines from the 2019 vintage, free guaiacol ranged from 1.2–2.3 $\mu\text{g/L}$ approximately 3 months after harvest (Figure 2).

Free guaiacol increased significantly from more recent to older vintages (Table 1). This baseline increase in guaiacol is important to note, as winemakers who track wines over time may misinterpret the result as smoke glycosides being released into their free form. Other free volatile phenolic compounds measured either only slightly increased over this time or remained constant. This result is consistent with previous research, which also saw an increase in smoke marker volatiles during bottle aging of wines not exposed to smoke.¹⁵

Neither vineyard location (AVA) nor rootstock were significant for the concentration of smoke marker compounds. In this survey, only 2–3 vineyards were selected per AVA, so significant trends may emerge if increased vineyard sites were studied. While AVA was not significant, wines from one vineyard site were statistical outliers for guaiacol in certain years (Grubbs test; $p < 0.0001$). There was also an approximately 1.85-fold difference in both free and total guaiacol across all sites (Figure 2). Therefore, it is still important for wineries to understand the range of baseline values for their own vineyard sites.

Unlike free volatile phenols, the concentration of total volatile phenols either did not change due to vintage or did not increase in a consistent manner. Total guaiacol largely did not change from 2016–2019 but was significantly higher in 2015. This result was unexpected, but an extremely hot and dry growing season in 2015, and relatively early harvest, may explain the increased concentrations in natural precursors.

The ratio of free to total guaiacol increased over time and appeared to approach a ratio of 1:2 (Figure 3). While this trend is in non-smoked wines, it may suggest that the worst-case

scenario for smoke tainted wine would be equal parts free and bound after 5 years. However, this trend needs further investigation.

The ratio between free guaiacol and 4-methylguaiacol has previously been found to be 3.7:1 in wine made from smoke impacted grapes.¹³ Wines in contact with oak tend to have higher concentrations of 4-methylguaiacol, depending on toast level, shifting this ratio down.¹⁷ Baseline wine samples studied here had a range of guaiacol:4-methylguaiacol ratios of 4.1–26.9. The average ratio did increase over time as free guaiacol increased faster than free 4-methylguaiacol (Table 2). The average ratio in 2019 wines was 6.0 ± 0.3 . Since this ratio was higher than what is typically observed in smoke impacted wine, it may be a valuable parameter to monitor when determining if results are due to baseline or smoke impact for a particular variety on a specific site.

Broader Impact

Smoke taint is a complex topic and years of research from across the world has helped further the industry's understanding of it. Significant strides have been made in identifying marker compounds, glycoconjugates, and vineyard conditions responsible for smoke impact. However, the wine industry is still in need of practical techniques to determine if a wine has been exposed to smoke and if that exposure will lead to perceptible quality changes. Many times, winemakers are faced with deciding whether to harvest fruit or to bottle wine without knowing the entire extent of the exposure. Becoming familiar with background levels of marker compounds is one avenue where winemakers can make more informed decisions.

This study examined baseline concentrations in Pinot noir c. 667 grown along the West Coast of the United States. Baseline volatile phenol concentrations will likely change by varietal,

as Syrah has already been demonstrated to contain between 20–40 µg/L free guaiacol.¹³ Other growing factors may also influence baseline concentrations, such as clone, or farming practices such as vine water status. For example, one vineyard site studied here was consistently an outlier with high guaiacol concentrations over multiple years. In 2015, which experienced hot and dry growing conditions, this site (RRV3) reached 30 Brix in August and experienced shrivel. While the fruit had a water addition prior to fermentation, adjusting for any shrivel concentration effects or increased alcohol extraction, the guaiacol concentration was still measured at 23 µg/L at the time of analysis. This result suggests that growing conditions have a large impact on baseline concentrations. Additionally, winemaking protocols may influence extraction from the berries. Since all these factors are likely to be different for individual vineyards and wineries, it is important for each winery to test baseline concentrations in a subset of the wines produced.

Early on in smoke taint research it was established that neither guaiacol nor 4-methylguaiacol were solely responsible for smoke taint aroma.¹⁸ However, guaiacol and 4-methylguaiacol are the most common marker compounds examined because they often increase the greatest after exposure to smoke and correlate strongly to sensory descriptors of smoke, burnt rubber, and leather.^{8,19} Many winemakers are familiar with guaiacol and 4-methylguaiacol concentrations when making inferences to smoke character. However, many commercial laboratories are now offering additional compounds, such as *m*-, *o*-, and *p*-cresol, which leads winemakers to question how to interpret these new results. Understanding the baseline of these additional compounds can help winemakers identify years when concentrations of these compounds spike.

Sensory thresholds for compounds commonly implicated in smoke exposure are one of the most sought-after pieces of information by winemakers. In 2012, Parker et al.⁸ established

best-estimate thresholds for guaiacol (23 µg/L), *m*-cresol (20 µg/L), *p*-cresol (64 µg/L), and *o*-cresol (62 µg/L). However, during sensory analysis wines were rated as smoke tainted while having concentrations under these thresholds, which pointed to either an additive or synergistic effect of these compounds, or to smoke aroma also stemming from unidentified compounds.⁸ This unknown factor of smoke taint sensory analysis has led commercial laboratories and other groups to make recommendations about smoke exposure at much lower concentrations than their reported thresholds, such as 4 µg/L guaiacol in whites and 6 µg/L in reds.¹³ As mentioned previously, the narrow range between baseline levels and potential smoke impact make it difficult for winemakers to assess risk. However, once ranges of baseline concentrations are known for wines from a given vineyard or region and variety, it would be possible to assign risk levels on the basis of how far the result is from historical baseline results. This classification system of risk would eliminate some of the ambiguity winemakers face when interpreting results, especially in fire damage years. This could potentially establish quality limits for discussions related to insurance claims or grower contracts.

Another beneficial feature to reduce uncertainty of smoke volatiles results, would be to find a marker compound that is not naturally present from grapes and only increased, even in small proportions, when smoke was present. From the results of this survey, 4-ethylguaiacol could potentially be a good candidate in Pinot noir due extremely low baseline concentrations (generally below 0.1 µg/l), and very little bound fraction released by acid hydrolysis (below 0.5 µg/L). Previous research has found increased 4-ethylguaiacol concentrations in smoked wines and non-detected levels in control wines.^{1,3,20} However, since 4-ethylguaiacol can also be formed from *Brettanomyces* growth in wines, the results would need to be interpreted carefully. Other possibilities for smoke markers could be the ratio between guaiacol and 4-methylguaiacol, or the

ratio between free and total guaiacol. However, these proposed parameters would require more extensive research to establish a correlation to smoked or non-smoked wines.

One main issue with assessing smoke risk during wine maturation is the release of bound compounds into their free forms over time. Acid hydrolysis is one technique for measuring the glycoconjugate fraction of smoke phenolics, which aggressively releases glycoconjugates to their free volatile phenol form. This protocol, which temporarily shifts the pH to 1.5, likely overestimates the quantity of free smoke markers that will be released at juice pH, because conditions in juice and wine are less extreme. Nevertheless, it does give an estimate of total risk and the extent of smoke exposure. In this study, approximately half of the total (free and bound) guaiacol was in the free form after 5 years. This could indicate an equilibrium between free and bound forms. However, past research has seen a variable rate of release of glycoconjugates over time depending on varietal and vintage.¹⁵ Additionally, most previous research has only seen a maximum increase in free guaiacol of 6 µg/L over time, even when pools of glycoconjugates are much larger, suggesting the equilibrium between free and bound may be more stable than what is observed in this study.^{11,15}

Experimental Design

Winemaking

Winemaking followed the protocol by Grainger et al.²¹ Briefly, grape clusters produced by *Vitis vinifera* L. cv. Pinot noir clone Dijon 667 were harvested from fourteen different vineyard sites. The sites represented eight different American Viticultural Areas (AVAs), which included Santa Rita Hills, Santa Maria Valley, Arroyo Seco, Carneros, Sonoma Coast, Russian River Valley, Anderson Valley, and Willamette Valley (OR).

Grapes were hand harvested at approximately 24 Brix. The grapes were destemmed but not crushed into 200 L stainless steel fermentors containing ca. 130 L of must. Wines were fermented in quadruplicate at the UC Davis Teaching & Research Winery (University of California, Davis, CA). Must was chilled to 7°C for a three-day cold soak. Wine was warmed to 21°C prior to inoculation with RC212 (Lallemand), which had been rehydrated with SuperStart Rouge (Laffort) according to the manufacturer's recommendation. The must nitrogen was adjusted with a combination of NutriStart (Laffort) and diammonium phosphate (DAP) when the yeast assimilable nitrogen (YAN) was less than 250 mg/L. Nutristart was used to provide 35 g YAN/hL, with DAP used to supply the remaining difference. The fermentation temperature was held at 21°C for two days following inoculation, and then was allowed to rise to 27°C and maintained at this temperature for the remainder of fermentation. Automated pump-overs were utilized to maintain the temperature setpoint. Wines were pressed on the ninth day after destemming. Wines were cooled to 18°C and inoculated with 100 mg/L Lalvin VP41 malolactic bacteria (Lallemand). After malolactic fermentation completed, the wines were chilled to 13°C and potassium metabisulfite was added to adjust molecular SO₂ to 0.6 mg/L. Wines were bottled approximately 6 months after harvest. Fermentation replicates were blended after the completion of malolactic fermentation.

Wines were made following the above procedure during the 2015–2019 vintages. Chemical analysis was performed in February 2020, making the wines 0.5–4.5 years old at the time of analysis. Wines from the 2019 vintage were analyzed from keg samples, while wines from 2015–2018 were analyzed as bottle samples, which were sealed under screw-cap closure.

Chemical Analysis

Acid hydrolysis is one technique to release and then measure all glycosylated volatile phenols. Acid hydrolysis was performed according to Noestheden et al.²² Briefly, 14 mL of wine was added to a 20 mL borosilicate glass vial. Guaiacol d₃ was added as an extraction surrogate at a rate of 10 µg/L. Hydrochloric acid (HCl) was added until the pH reached 1.5. The wine was then heated to 100°C for 4 hours. After 4 hours, the sample was immediately chilled to room temperature. The wine was adjusted back to the original pH with 4N sodium hydroxide (NaOH) to make sample handling safer. Dilution from HCl and NaOH was accounted for in data analysis.

GC-MS/MS

A 10 mL sample of either wine or wine after acid hydrolysis was pipetted to a GCMS vial. For free samples, both 4-methylguaiacol d₃ and guaiacol d₃ were added at a rate of 10 µg/L as internal standards. For acid hydrolysis samples, only 4-methylguaiacol d₃ was added as guaiacol d₃ was already used as a surrogate. Salt (2 g) was then added to help force aromatic compounds into the headspace. Samples were mixed until salt dissolved.

SPME (DVB/CAR/PDMS; 50/30 µm, 23 Ga) sampling was utilized. While many researchers have recently begun using SPE and liquid injection,⁶ we chose to use SPME to more closely match protocols from commercial laboratories servicing the industry. The sample was incubated at 60°C for 3 minutes, and then extracted for 30 minutes at 60°C. Desorption time was 5 minutes, and the inlet temperature was 250°C. Injection was splitless. GC column was TG-WAXMS (30m x 0.25mm ID x 0.25 µm film; Thermo Scientific). Carrier gas flow rate was 1.2 mL/min. Oven temperature started at 40°C, held at this temperature for 4 minutes, increased to

100°C at 12°C/min, then increased to 160°C at 15°C/min, then increased to 250°C at 20°C/min and held at this temperature for 8.5 minutes.

Detection was carried out with selected reaction monitoring (SRM). MS transfer line was held at 250°C and the ion source was held at 220°C. Method validation was carried out and reproducibility was less than 8% RSD for all compounds in both free volatile and acid hydrolysis samples.

Volatile phenol standards were purchased as a 1 g/L mixture from Absolute Standards, Inc. (Hamden, CT).

Statistical Analysis

Data analysis was performed in XLSTAT. Analysis of variance (ANOVA) was performed for vintage, AVA, and rootstock for each measured compound. Fisher's Least Significant Difference (LSD) was used for comparison of means.

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Table and Figure Captions

Table 1. Average concentration of free and total acid hydrolysis volatiles over 5 vintages of Pinot noir. Data presented as mean \pm standard error. Data not sharing a letter are significantly different at $p < 0.05$ (Fisher LSD). N.D. indicates compound not detected (limit of detection-0.1 $\mu\text{g/L}$) and N/A represents compounds degraded during acid hydrolysis.

Table 2. Ratio of guaiacol to 4-methylguaicol increased over time. Data presented as mean \pm standard error. Data not sharing a letter are significantly different at $p < 0.05$ (Fisher LSD).

Figure 1. Fruit was harvested from 15 vineyard sites across California and Oregon over five years (2015-2019). Vineyard sites were within latitudes of 34° and 45° North and within longitudes of 120° and 123° West.

Figure 2 Free (A) and total (B) guaiacol from 2019 wines by vineyard site. Sites are labeled as AVA and vineyard number (AS-Arroyo Seco; AV-Anderson Valley; CRN-Carneros; OR-Oregon; RRV-Russian River Valley; SMV-Santa Maria Valley; SNC-Sonoma Coast; SRH-Santa Rita Hills).

Figure 3. The ratio of free to total (acid hydrolysis released) guaiacol increases with wine age. Data presented as mean \pm standard error, significance established with Fisher's LSD; $p < 0.05$.

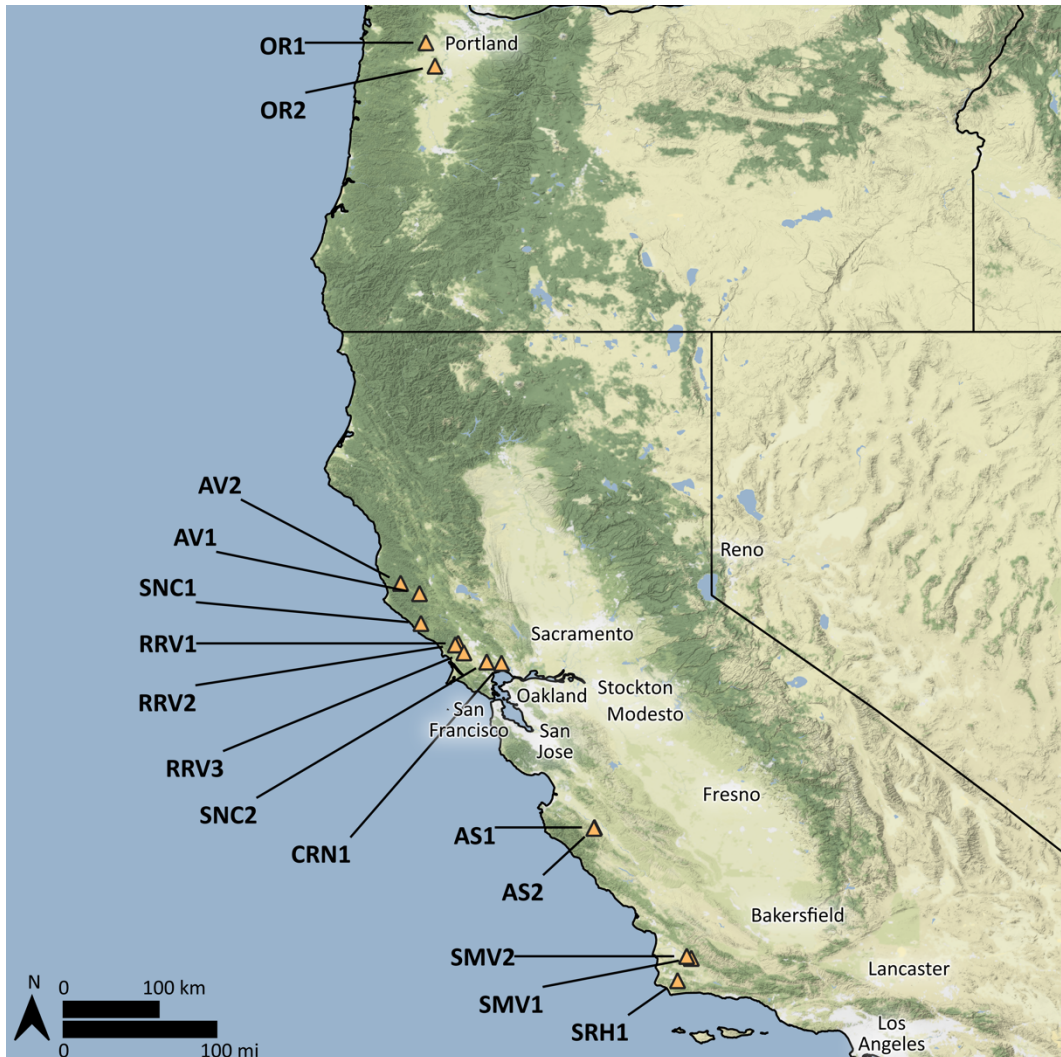
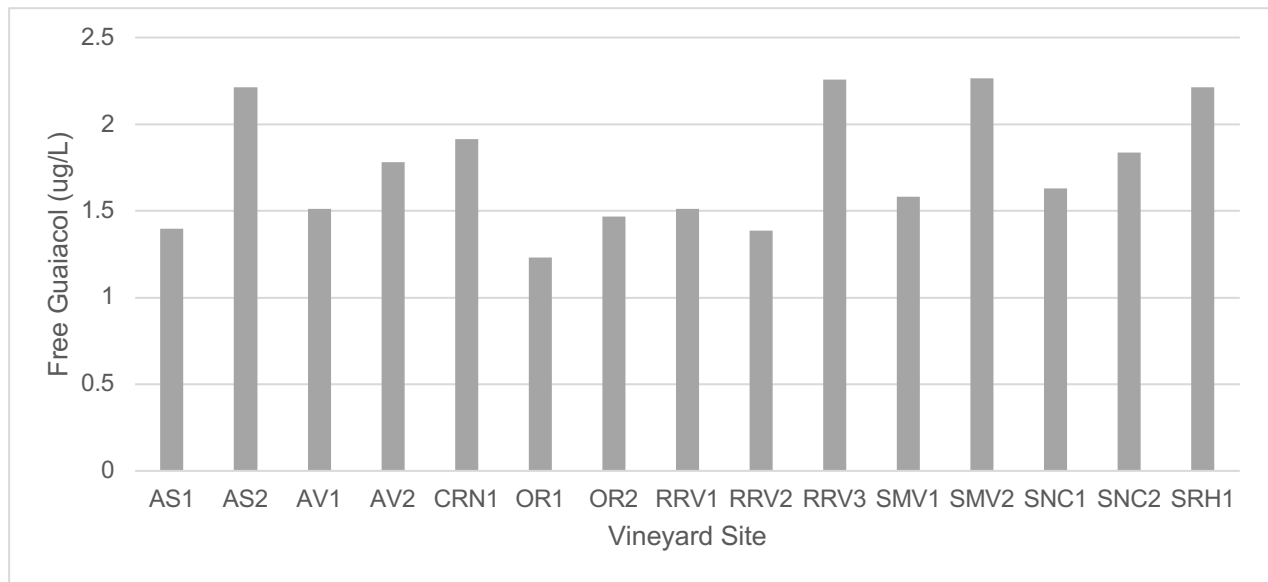


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A.



B.

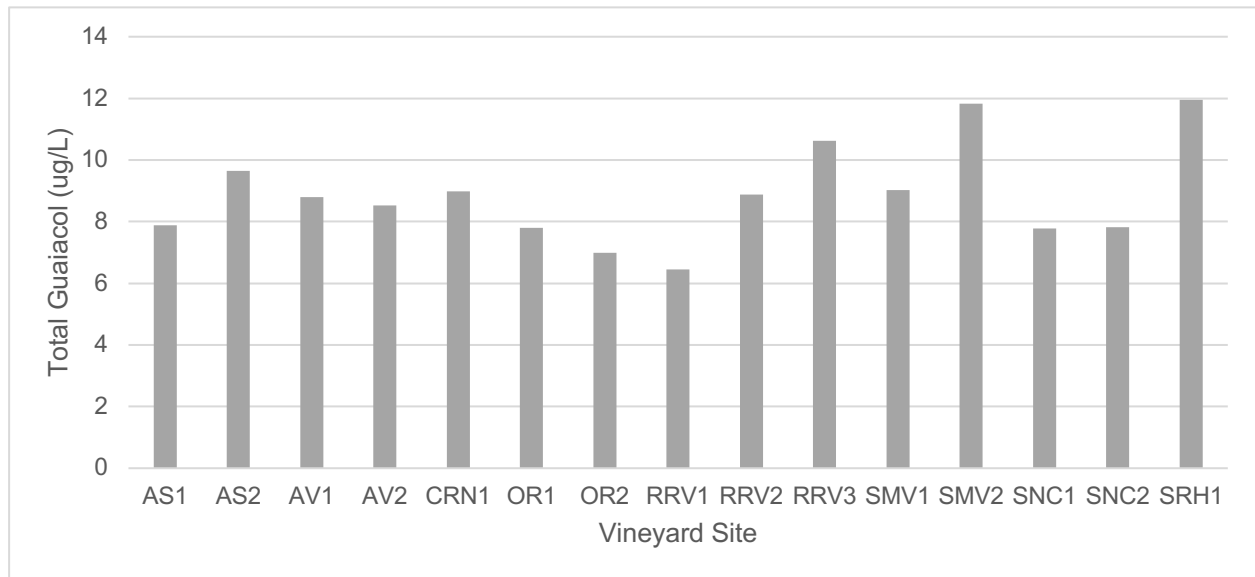


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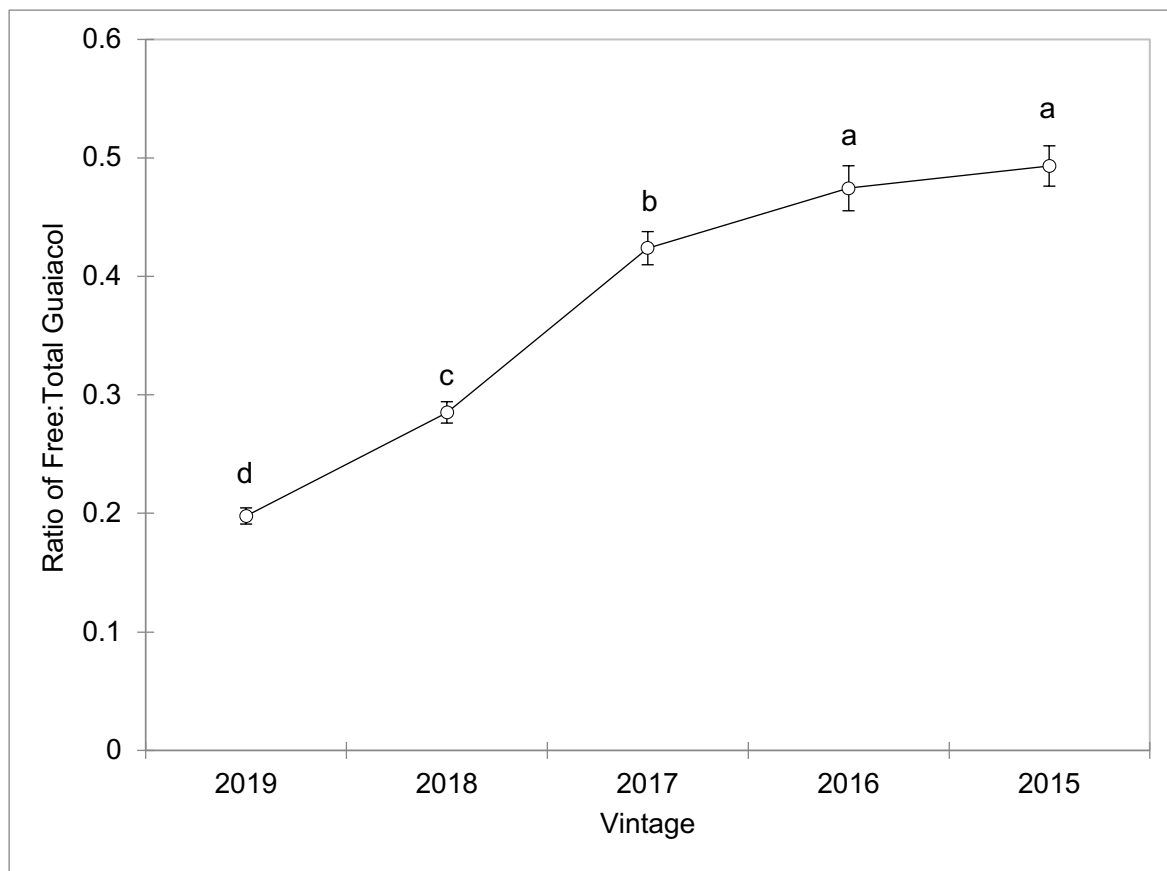


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<u>Free Volatiles ($\mu\text{g/L}$)</u>							
Vintage	Guaiacol	4-Methylguaiacol	4-Ethylguaiacol	4-Ethylphenol	<i>m</i>-cresol	<i>o</i>-cresol	<i>p</i>-cresol
2019	1.7 \pm 0.1 d	0.29 \pm 0.01 b	0.04 \pm 0.04	0.30 \pm 0.02 c	1.0 \pm 0.1	1.8 \pm 0.1 b	1.3 \pm 0.1 b
2018	2.6 \pm 0.2 cd	0.30 \pm 0.02 b	0.01 \pm 0.01	0.50 \pm 0.06 b	1.0 \pm 0.1	1.8 \pm 0.1 b	1.8 \pm 0.2 ab
2017	4.1 \pm 0.3 bc	0.40 \pm 0.03 a	N.D.	0.52 \pm 0.03 b	1.1 \pm 0.1	2.1 \pm 0.1 ab	1.8 \pm 0.3 ab
2016	4.6 \pm 0.5 c	0.39 \pm 0.02 a	0.01 \pm 0.01	0.80 \pm 0.07 a	1.2 \pm 0.1	2.4 \pm 0.2 a	2.2 \pm 0.3 a
2015	8.9 \pm 1.2 a	0.46 \pm 0.04 a	0.02 \pm 0.02	0.85 \pm 0.07 a	1.2 \pm 0.1	2.3 \pm 0.1 a	2.2 \pm 0.2 a
<u>Total (Acid Hydrolysis) Volatiles ($\mu\text{g/L}$)</u>							
Vintage	Guaiacol	4-Methylguaiacol	4-Ethylguaiacol	4-Ethylphenol	<i>m</i>-cresol	<i>o</i>-cresol	<i>p</i>-cresol
2019	8.9 \pm 0.4 b	1.38 \pm 0.03 c	0.30 \pm 0.06 ab	2.3 \pm 0.1 c	N/A	3.6 \pm 0.2	N/A
2018	9.1 \pm 0.6 b	1.49 \pm 0.04 bc	0.35 \pm 0.04 ab	3.2 \pm 0.2 a	N/A	3.4 \pm 0.2	N/A
2017	9.9 \pm 0.8 b	1.51 \pm 0.04 bc	0.24 \pm 0.04 bc	2.6 \pm 0.2 b	N/A	3.6 \pm 0.2	N/A
2016	9.5 \pm 0.7 b	1.59 \pm 0.07 b	0.14 \pm 0.03 c	2.1 \pm 0.1 c	N/A	3.7 \pm 0.3	N/A
2015	17.3 \pm 1.5 a	1.81 \pm 0.11 a	0.37 \pm 0.04 a	3.1 \pm 0.1 a	N/A	3.3 \pm 0.2	N/A

Table 2. Ratio of guaiacol to 4-methylguaiacol increased over time. Data presented as mean \pm standard error. Data not sharing a letter are significantly different at $p < 0.05$ (Fisher LSD).

Vintage	Guaiacol:4-methylguaiacol
2019	6.0 \pm 0.3 d
2018	8.8 \pm 0.6 c
2017	10.7 \pm 0.6 bc
2016	11.8 \pm 0.8 b
2015	18.8 \pm 1.1 a