

ASEV CATALYST REPORT

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

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Summary

Goals: With increased wildfires in recent years, winemakers now regularly need to interpret results from analyses for smoke related marker compounds to determine if smoke intrusion has impacted their wines. The goal of this study was to examine naturally occurring baseline levels of smoke exposure marker compounds in un-oaked Pinot noir to enable winemakers to better understand smoke exposure 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*-,

26 *p*-, and *o*-cresol. In 2019, the baseline free guaiacol concentration ranged from 1.2–2.3
27 µg/L, while total (free and bound) guaiacol ranged from 6.4–12.0 µg/L.

- 28 • The concentration of free guaiacol was greater in older vintages, while total guaiacol
29 largely did not change from year to year.
- 30 • The ratio of free to total guaiacol approached 1:2 after 5 years, suggesting baseline
31 guaiacol may approach an equal ratio of free to bound over time.

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

39 **Key words:** analysis, aroma, guaiacol, Pinot noir, smoke exposure

40 **Overview**

41 Wildfire smoke has caused concern for wine quality around the world in the last two
42 decades. As fires burn, volatile phenols are generated from the breakdown of lignin. Depending
43 on the wood source, different types of volatile phenols are also present in the smoke.¹ These
44 volatile phenols are then taken up by the plant, either directly through the fruit, or through the
45 leaves and translocated to the fruit.² Although multiple compounds are responsible for smoke
46 aroma, guaiacol and 4-methylguaiacol are often used as key exposure markers because they are

47 typically found in the highest quantities in smoke exposed grapes and wines.³ Other compound
48 classes implicated in smoke exposure aroma include syringyls (syringols), *p*-hydroxy-phenyls
49 (phenols and cresols), and guaiacyls (guaiacols and eugenol).¹ Baseline concentrations of these
50 compounds in different wine varieties need to be established to better understand risk attributed
51 to smoke exposure during smoke impacted vintages.

52 When volatile phenolics are taken up by the plant, they are bound to sugar molecules to
53 minimize the toxic effect on the plant.^{3,4} Many researchers are currently examining exactly
54 which of these glycoconjugates form and how these compounds change over time in
55 winemaking.^{5,6} However, due to a wide range of compounds present, this approach can be
56 challenging for commercial laboratories to use as a screening tool for routine analysis. Acid or
57 enzyme hydrolysis are techniques used to estimate the concentrations of this group of
58 compounds by releasing them into their free volatile form.³ Because sample analysis by acid or
59 enzyme hydrolysis measures both initially free volatiles and volatile compounds released
60 through the hydrolysis process, the protocol estimates the total pool of smoke phenolics present
61 in a wine. While there are drawbacks to both acid and enzyme hydrolysis, including the
62 formation of artifacts, acid hydrolysis has been found to be more reflective of grape and wine
63 aroma than enzyme hydrolysis.⁷

64 Free volatile phenols are primarily responsible for smoke taint aroma and flavor,⁸ while
65 glycosylated compounds contribute to smoke flavor and aftertaste.^{2,9} One sensory study reported
66 the strongest smoke flavor was found in wines spiked with both free volatiles and glycosylated
67 smoke-related compounds.⁹ Bound compounds may also hydrolyze to release their free volatile
68 form during aging of a wine, making smoke aroma worse over time.¹⁰ This temporal change in

69 free volatile phenolics has been most significantly noted regarding mitigation efforts, such as
70 when wines are treated with reverse osmosis filtration, but smoke aroma returns over time.¹¹ Due
71 to the overall sensory impact of both free and bound compounds, it is important to measure both
72 fractions to assess the immediate smoke impact as well as the potential long-term risk.

73 Additionally, it is important to be familiar with baseline concentrations of both free and
74 bound compounds to properly understand risk. Free and bound guaiacol has been previously
75 identified in non-smoked Merlot, Cabernet Sauvignon, Syrah, Tempranillo, Grenache, and
76 Viognier.^{3,12-15} Many of the baseline concentrations currently published are from control wines in
77 smoke exposure research. For example, a non-smoked Merlot wine was reported to have 4 µg/L
78 guaiacol, and trace levels (less than 1 µg/L) of 4-ethylguaiacol, 4-ethylphenol, and eugenol.^{1,3}
79 While these concentrations are often many orders of magnitude lower than concentrations for
80 smoked fruit and wines reported in literature, a commercial lab has reported their observations
81 that red wines with free guaiacol concentrations over 6 µg/L lead to smoky aromas;¹³ a limitation
82 of this report is that it lacks a controlled sensory evaluation and the rigor of peer review. With
83 such a narrow margin between normal and potentially smoke impacted results, winemakers will
84 be better prepared to make risk assessments if they are aware of the typical baseline
85 concentration in their own wines.

86 To date, baseline concentrations of smoke volatile phenols are not widely available.
87 Researchers at AWRI (Australian Wine Research Institute) have conducted an intensive baseline
88 survey, but this data has not yet been published.¹⁶ Additionally, there is a limited understanding
89 of the impact of growing conditions and site on the level of baseline concentrations. This study
90 aims to examine baseline concentrations of common smoke exposure marker compounds in

91 Pinot noir wines from 15 different vineyard sites in California and Oregon. This study also aims
92 to compare concentrations of these compounds in wines at various stages of aging, so that
93 winemakers can better interpret the relative impacts on their wines at any stage of maturation.
94 Thus, allowing for better interpretation of general risk when fires erupt in their winegrowing
95 regions.

96 Major Observations and Interpretations

97 Pinot noir wines produced over 5 vintages (2015–2019) from California and Oregon were
98 examined at the same time-point (February 2020) for volatile smoke compounds including
99 guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-ethylphenol, and *m*-, *o*-, and *p*-cresol. Thirteen
100 vineyard sites were analyzed in California and two were analyzed in Oregon (Figure 1). Over
101 those five vintages, only one wine from 2018 was excluded due to potential environmental
102 smoke impact as a result of its elevation (ca. 500 m), even though the smoke would have drifted
103 more than 150 km. While there were other fires in California and Oregon between 2015-2019,
104 vineyards were either not impacted due to geographical location or harvested prior to smoke
105 impact (Table S1). In all years, concentrations of both free and total volatile phenolic compounds
106 were measured. For clarity, we will use the terminology ‘total’ to refer to the concentration after
107 acid hydrolysis. Additionally, in this study *p*- and *m*-cresol both showed loss of peak resolution
108 after acid hydrolysis and were therefore only included in the free volatile data analysis.

109 Pinot noir wines from various regions in California and the Willamette Valley of Oregon
110 had detectable baseline levels of all measured smoke volatile phenols, except 4-ethylguaiacol
111 (Table 1). The concentration of all free volatile phenols was relatively low. In wines from the
112 2019 vintage, free guaiacol ranged from 1.2–2.3 µg/L approximately 3 months after harvest

113 (Figure 2). There was a similar range in cresol isomers by site, with a minimum of 0.6 $\mu\text{g/L}$ in
114 m-cresol, and a maximum of 2.8 $\mu\text{g/L}$ in p-cresol (Figure 2).

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

121 Neither vineyard location (AVA) nor rootstock were significant for the concentration of
122 smoke marker compounds. In this survey, only 2–3 vineyards were selected per AVA, so
123 significant trends may emerge if increased vineyard sites were studied. While AVA was not
124 significant, wines from one vineyard site were statistical outliers for guaiacol in certain years
125 (Grubbs test; $p < 0.0001$). The outlier vineyard site was not smoke affected in any year studied,
126 but did experience berry dehydration, and subsequently high Brix, before it was harvested. There
127 was also approximately a 1.85-fold difference in both free and total guaiacol across all sites
128 (Figure 2). Therefore, it is still important for wineries to understand the range of baseline values
129 for their own vineyard sites.

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

135 The ratio of free to total guaiacol increased over time and appeared to approach a ratio of
136 1:2 (Figure 3). While this trend is in non-smoked wines, it may suggest that the worst-case
137 scenario for smoke tainted wine would be equal parts free and bound after 5 years. However, this
138 trend needs further investigation.

139 In studies that report detectable levels of both guaiacol and 4-methylguaiacol, the
140 calculated ratio between free guaiacol to free 4-methylguaiacol ranges from 3.7–4.5 in finished
141 wines.^{3,13,17,18} However in one study, this ratio was reported as high as 5.8 in wines just finishing
142 primary fermentation.³ Wines in contact with oak tend to have higher concentrations of 4-
143 methylguaiacol, depending on toast level, shifting this ratio down.¹⁹ Baseline wine samples
144 studied here had a range of guaiacol:4-methylguaiacol ratios of 4.1–26.9. The average ratio did
145 increase over time as free guaiacol increased faster than free 4-methylguaiacol (Table 2). The
146 average ratio in 2019 wines was 6.0 ± 0.3 . Since this ratio was higher than what has been
147 observed in smoke impacted wine, it may be a valuable parameter to monitor when determining
148 if results are due to baseline or smoke impact for a particular variety on a specific site.

149 **Broader Impact**

150 Smoke taint is a complex topic and years of research from across the world has helped
151 further the industry's understanding of it. Significant strides have been made in identifying
152 marker compounds, glycoconjugates, and vineyard conditions responsible for smoke impact.
153 However, the wine industry is still in need of practical techniques to determine if a wine has been
154 exposed to smoke and if that exposure will lead to perceptible quality changes. Many times,
155 winemakers are faced with deciding whether to harvest fruit or to bottle wine without knowing

156 the entire extent of the exposure. Becoming familiar with background levels of marker
157 compounds is one avenue where winemakers can make more informed decisions.

158 This study examined baseline concentrations in Pinot noir c. 667 grown along the West
159 Coast of the United States. Baseline volatile phenol concentrations will likely change by varietal,
160 as Syrah has already been reported to contain between 20–40 µg/L free guaiacol.¹³ Other
161 growing factors may also influence baseline concentrations, such as clone, or farming practices
162 such as vine water status. For example, one vineyard site studied here was consistently an outlier
163 with high guaiacol concentrations over multiple years. In 2015, which experienced hot and dry
164 growing conditions, this site (RRV3) reached 30 Brix in August and experienced shrivel. While
165 the fruit had a water addition prior to fermentation, adjusting for any shrivel concentration
166 effects or increased alcohol extraction, the guaiacol concentration was still measured at 23 µg/L
167 at the time of analysis. This result suggests that growing conditions can have a large impact on
168 baseline concentrations. Additionally, winemaking protocols may influence extraction from the
169 berries. Because all these factors are likely to be different for individual vineyards and wineries,
170 it is important for each winery to test baseline concentrations in a subset of the wines produced.

171 Guaiacol and 4-methylguaiacol are the most common marker compounds examined as
172 baseline marker compounds. They often show the greatest increase after exposure to smoke and
173 correlate strongly to sensory descriptors of smoke, burnt rubber, and leather.^{8,20} Early on in
174 smoke taint research it was established, however, that neither guaiacol nor 4-methylguaiacol
175 were solely responsible for smoke taint aroma.¹⁷ Many winemakers are therefore familiar with
176 guaiacol and 4-methylguaiacol concentrations when making inferences to smoke character.
177 However, many commercial laboratories are now offering additional compounds, such as *m*-, *o*-,

178 and *p*-cresol, which leads winemakers to question how to interpret these new results.
179 Understanding the baseline of these additional compounds can help winemakers identify years
180 when concentrations of these compounds spike.

181 Sensory thresholds for compounds commonly implicated in smoke exposure are one of
182 the most sought-after pieces of information by winemakers. In 2012, Parker et al.⁸ established
183 best-estimate thresholds for guaiacol (23 µg/L), *m*-cresol (20 µg/L), *p*-cresol (64 µg/L), and *o*-
184 cresol (62 µg/L). However, during sensory analysis wines were rated as smoke exposed while
185 having concentrations under these thresholds, which pointed to either an additive or synergistic
186 effect of these compounds, or to smoke aroma also stemming from unidentified compounds.⁸
187 This unknown factor of smoke impact sensory analysis has led commercial laboratories and
188 other groups to make recommendations about smoke exposure at much lower concentrations
189 than their reported thresholds, such as 4 µg/L guaiacol in whites and 6 µg/L in reds.¹³ As
190 mentioned previously, the narrow range between baseline levels and potential smoke impact
191 make it difficult for winemakers to assess risk. However, once ranges of baseline concentrations
192 are known for wines from a given vineyard or region and variety, it would be possible to assign
193 risk levels on the basis of how far the result is from historical baseline results. This
194 classification system of risk would eliminate some of the ambiguity winemakers face when
195 interpreting results, especially in fire damage years. This could potentially establish quality limits
196 for discussions related to insurance claims or grower contracts.

197 Another beneficial feature to reduce uncertainty of smoke volatiles results, would be to
198 find a marker compound that is not naturally present from grapes and only increased, even in
199 small proportions, when smoke was present. From the results of this survey, 4-ethylguaiacol

200 could potentially be a good candidate in Pinot noir due extremely low baseline concentrations
201 (generally below 0.1 $\mu\text{g/l}$), and very little bound fraction released by acid hydrolysis (below 0.5
202 $\mu\text{g/L}$). However, preliminary research from the 2020 vintage indicates that the accumulation of
203 4-ethylguaiacol was very low in smoke impacted wines from California and Oregon (data not
204 shown). Previous research did find increased 4-ethylguaiacol concentrations in smoked wines
205 and non-detected levels in control wines,^{1,3,21} so further research will be important to establish a
206 clear relationship. Additionally, since 4-ethylguaiacol can also be formed from *Brettanomyces*
207 growth in wines, the results would need to be interpreted carefully. Other possibilities for smoke
208 markers could be the ratio between guaiacol and 4-methylguaiacol, or the ratio between free and
209 total guaiacol. However, these proposed parameters would require more extensive research to
210 establish a correlation to smoked or non-smoked wines.

211 One main issue with assessing smoke risk during wine maturation is the release of bound
212 compounds into their free forms over time. Acid hydrolysis is one technique for measuring the
213 glycoconjugate fraction of smoke phenolics. The method uses a combination of low pH and heat
214 to effectively release glycoconjugates to their free volatile phenol form. Since this method
215 temporarily shifts the pH to 1.5, it likely overestimates the quantity of free smoke markers that
216 will be released at juice pH, because conditions in juice and wine are less extreme. Additionally,
217 acid hydrolysis does introduce the risk of creating artifacts, as aglycones can re-arrange at low
218 pH.²² Nevertheless, it does give an estimate of total risk and the extent of smoke exposure. In this
219 study, approximately half of the total (free and bound) guaiacol was in the free form after 5
220 years. Past research has seen a variable, but generally slow, rate of release of glycoconjugates
221 over time depending on varietal and vintage.¹⁵ Additionally, previous research has only reported

222 a maximum increase in free guaiacol of 6 $\mu\text{g/L}$ over time, even when pools of glycoconjugates
223 are much larger, suggesting the release of bound to free may be more stable than what is
224 observed in this study.^{11,15}

225 **Experimental Design**

226 Winemaking

227 Winemaking followed the protocol by Grainger et al.²³ Briefly, grape clusters produced
228 by *Vitis vinifera* L. cv. Pinot noir clone Dijon 667 were harvested from fourteen different
229 vineyard sites. The sites represented eight different American Viticultural Areas (AVAs), which
230 included Santa Rita Hills, Santa Maria Valley, Arroyo Seco, Carneros, Sonoma Coast, Russian
231 River Valley, Anderson Valley, and Willamette Valley (OR).

232 Grapes were hand harvested at approximately 24 Brix. The grapes were destemmed but
233 not crushed into 200 L stainless steel fermentors containing ca. 130 L of must. Wines were
234 fermented in quadruplicate at the UC Davis Teaching & Research Winery (University of
235 California, Davis, CA). Must was chilled to 7°C for a three-day cold soak. Wine was warmed to
236 21°C prior to inoculation with RC212 (Lallemand), which had been rehydrated with SuperStart
237 Rouge (Laffort) according to the manufacturer's recommendation. The must nitrogen was
238 adjusted with a combination of NutriStart (Laffort) and diammonium phosphate (DAP) when the
239 yeast assimilable nitrogen (YAN) was less than 250 mg/L. Nutristart was used to provide 35 g
240 YAN/hL, with DAP used to supply the remaining difference. The fermentation temperature was
241 held at 21°C for two days following inoculation, and then was allowed to rise to 27°C and
242 maintained at this temperature for the remainder of fermentation. Automated pump-overs were
243 utilized to maintain the temperature setpoint. Wines were pressed on the ninth day after

244 destemming. Wines were cooled to 18°C and inoculated with 100 mg/L Lalvin VP41 malolactic
245 bacteria (Lallemand). After malolactic fermentation completed, the wines were chilled to 13°C
246 and potassium metabisulfite was added to adjust molecular SO₂ to 0.6 mg/L. Wines were bottled
247 approximately 6 months after harvest. Fermentation replicates were blended after the completion
248 of malolactic fermentation.

249 Wines were made following the above procedure during the 2015–2019 vintages.

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

253 Chemical Analysis

254 Acid hydrolysis is one technique to release and then measure all glycosylated volatile
255 phenols. Acid hydrolysis was performed according to Noestheden et al.²⁴ Briefly, 14 mL of wine
256 was added to a 20 mL borosilicate glass vial. Guaiacol d₃ was added as an extraction surrogate at
257 a rate of 10 µg/L. Hydrochloric acid (HCl) was added until the pH reached 1.5. The wine was
258 then heated to 100°C for 4 hours. After 4 hours, the sample was immediately chilled to room
259 temperature. The wine was adjusted back to the original pH with 4N sodium hydroxide (NaOH)
260 to make sample handling safer. Dilution from HCl and NaOH was accounted for in data analysis.

261 GC-MS/MS

262 A 10 mL sample of either wine or wine after acid hydrolysis was pipetted to a GCMS
263 vial. For free samples, both 4-methylguaiacol d₃ and guaiacol d₃ were added at a rate of 10 µg/L
264 as internal standards. For acid hydrolysis samples, only 4-methylguaiacol d₃ was added as

265 guaiacol d₃ was already used as a surrogate. Salt (2 g) was then added to help force aromatic
266 compounds into the headspace. Samples were mixed until salt dissolved.

267 SPME (DVB/CAR/PDMS; 50/30 μm, 23 Ga) sampling was utilized. While many
268 researchers have recently begun using SPE and liquid injection,⁶ we chose to use SPME to more
269 closely match protocols from commercial laboratories servicing the industry. The sample was
270 incubated at 60°C for 3 minutes, and then extracted for 30 minutes at 60°C. Desorption time was
271 5 minutes, and the inlet temperature was 250°C. Injection was splitless. GC column was TG-
272 WAXMS (30m x 0.25mm ID x 0.25 μm film; Thermo Scientific). Carrier gas flow rate was 1.2
273 mL/min. Oven temperature started at 40°C, held at this temperature for 4 minutes, increased to
274 100°C at 12°C/min, then increased to 160°C at 15°C/min, then increased to 250°C at 20°C/min
275 and held at this temperature for 8.5 minutes.

276 Detection was carried out with selected reaction monitoring (SRM). MS transfer line was
277 held at 250°C and the ion source was held at 220°C. Method validation was carried out and
278 reproducibility was less than 10% RSD for all compounds in both wines and calibration
279 standards for free volatile and acid hydrolysis. Guaiacol reproducibility was very robust; 2.5%
280 RSD in standards, and 5.5% RSD in wines (n=6).

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

283 Statistical Analysis

284 Data analysis was performed in XLSTAT. Analysis of variance (ANOVA) was
285 performed for vintage, AVA, and rootstock for each measured compound. Fisher's Least

286 Significant Difference (LSD) was used for comparison of means. A two-sided Grubbs test for
287 outliers was performed at $p < 0.05$.

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Table 1 Average concentration of free and total acid hydrolysis volatiles over 5 vintages of Pinot noir wines. Data presented as mean \pm standard error. Data not sharing a letter are significantly different at $p < 0.05$ (Fisher LSD), $n=15$ in all years except 2018, where $n=14$ due to potential smoke exposure at one site. N.D. indicates compound not detected and N/A represents compounds not measured after acid hydrolysis.

Free Volatiles ($\mu\text{g/L}$)							
Vintage	Guaiacol	4-Methylguaiacol	4-Ethylguaiacol	4-Ethylphenol	<i>m</i> -cresol	<i>o</i> -cresol	<i>p</i> -cresol
Detection Limit	0.1	0.1	1.0	1.0	0.5	0.5	0.5
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
Total (Acid Hydrolysis) Volatiles ($\mu\text{g/L}$)							
Vintage	Guaiacol	4-Methylguaiacol	4-Ethylguaiacol	4-Ethylphenol	<i>m</i> -cresol	<i>o</i> -cresol	<i>p</i> -cresol
Detection Limit	0.1	0.1	1.0	1.0	0.5	0.5	0.5
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), $n = 15$ in all years except 2018, where $n = 14$ due to potential smoke exposure at one site.

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



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.

A

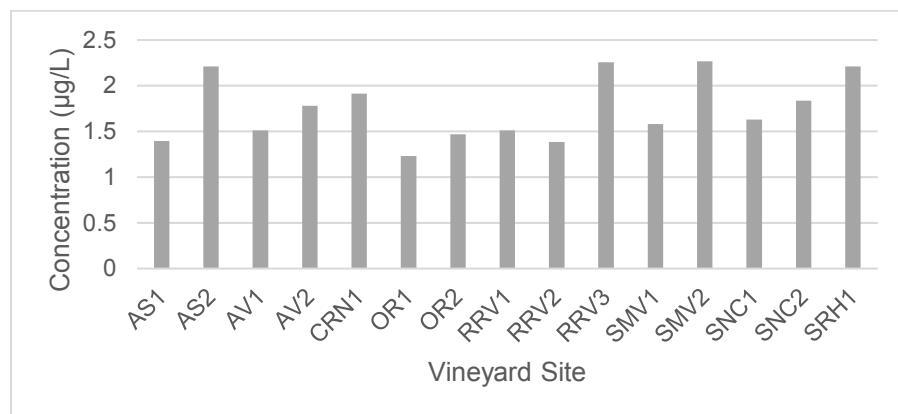
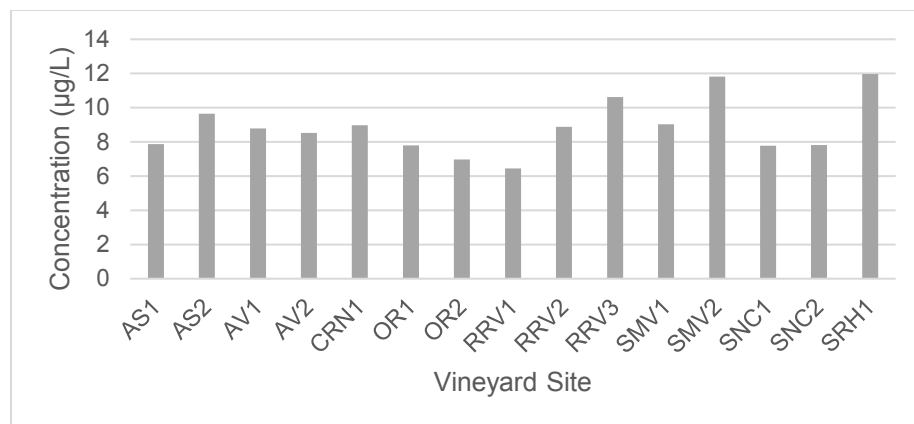
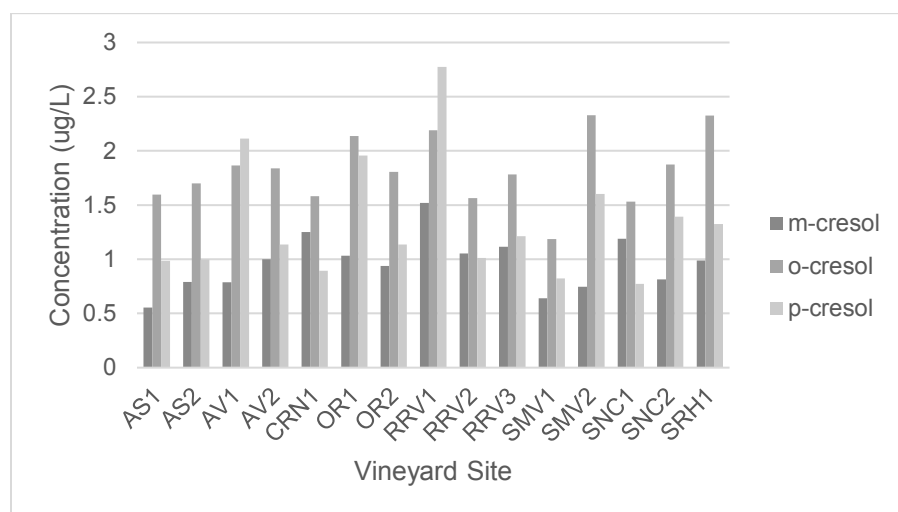


Figure 2 Free (A) and total (B) guaiacol, and free cresol isomers (C) from 2019 wines by vineyard site. Sites are labeled as AVA and vineyard number (AS-Arroyo Seco; AV-Anderson Valley; CRN-Carneros; OR-Oregon; RRV-Russian River Valley; SMV-Santa Maria Valley; SNC-Sonoma Coast; SRH-Santa Rita Hills).

B



C



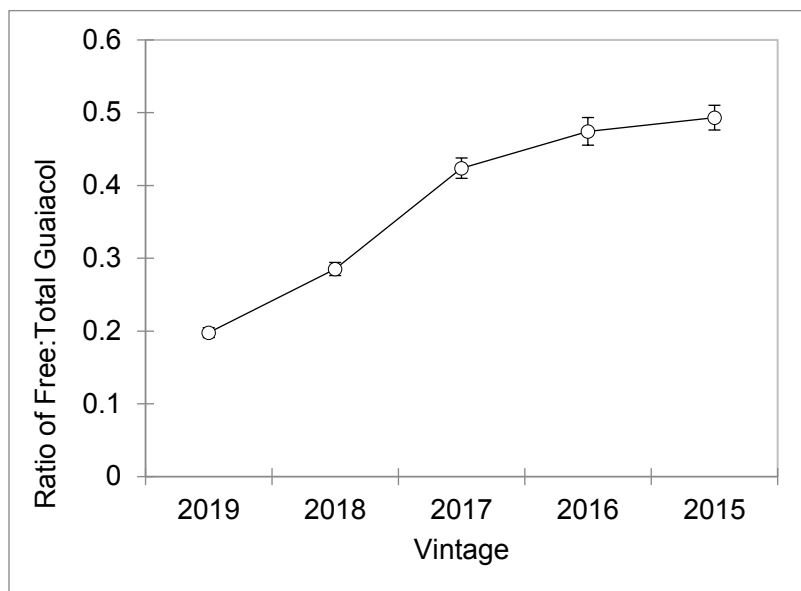


Figure 3 The ratio of free to total (acid hydrolysis released) guaiacol increases with wine age. Data presented as mean \pm standard error, significance established with Fisher's LSD; $p < 0.05$, $n = 15$ in all years except 2018, where $n = 14$ due to potential smoke exposure at one site.

Supplemental Table 1 Harvest dates by site and year show that each vineyard site was harvested prior to smoke impact.

Vineyard	Harvest Dates				
	2015	2016	2017	2018	2019
SRH1	9/14/2015	9/8/2016	9/8/2017	9/24/2018	9/24/2019
SMV1	8/20/2015	9/8/2016	9/4/2017	9/24/2018	9/24/2019
SMV2	8/13/2015	9/8/2016	9/4/2017	9/19/2018	9/24/2019
AS1	8/20/2015	8/25/2016	8/30/2017	9/11/2018	9/16/2019
AS2	8/20/2015	8/25/2016	8/30/2017	9/11/2018	9/16/2019
SNC1	9/3/2015	9/10/2016	9/6/2017	9/17/2018	9/13/2019
SNC2	8/19/2015	8/31/2016	8/31/2017	9/17/2018	9/10/2019
CRN1	8/19/2015	9/6/2016	8/31/2017	9/17/2018	9/4/2019
RRV1	9/3/2015	9/8/2016	9/6/2017	9/17/2018	9/10/2019
RRV2	9/3/2015	9/8/2016	9/5/2017	9/13/2018	9/16/2019
RRV3	9/10/2015	9/8/2016	9/13/2017	10/6/2018	9/18/2019
AV1	8/20/2015	9/6/2016	9/12/2017	10/8/2018	9/23/2019
AV2	9/15/2015	9/21/2016	9/25/2017	10/6/2018	9/23/2019
OR1	9/14/2015	9/16/2016	10/4/2017	9/29/2018	9/30/2019
OR2	9/14/2015	9/16/2016	10/4/2017	9/29/2018	9/30/2019