Grape smoke exposure risk assessment: Wine matrix impact on smoke marker compound smoke expression

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Abstract. During wildfires large amounts of volatile phenols (VP's) are released into the air from wood burning. These compounds absorb through the berry skin, where they are quickly glycosylated. Studies have shown that both the free and bound volatile phenols contribute to smoke taint perception. For grape smoke exposure risk assessment, both the natural amount of free and bound VP's in grapes (baseline) as well as rejection threshold levels of these compounds in different wine matrixes need to be determined. In the current study the sensory attributes of different smoke impacted and non-smoke impacted wines from the same sites were determined by descriptive analysis. Multivariate statistics were used to relate smoke-related sensory attributes to smoke marker compounds. Subsequently, wines with different levels of smoke marker compounds were made by serial dilution of a smoke impacted wine with its respective non-impacted wine. A consumer study was conducted to determine the change in 'liking' for a wine depending on the percentage inclusion of smoke impacted wine. Rejection threshold levels of smoke marker compounds in red wine matrixes were determined by linking 'liking' scores to specific wine attributes. This is the first step in creating clear guidelines for wine smoke taint risk assessment.

1 Introduction

The increasing incidences of wildfires in winegrape growing regions pose a significant risk to the grape and wine industry. Persistent exposure to smoke can compromise the quality and value of winegrapes and adversely affect wines made from smoke exposed grapes. A wine is seen as smoke impacted or tainted when there is an overpowering smoky, medicinal, chemical, burnt, or ashy aroma on the nose and a distinctive retronasal ash tray-like character in the mouth [1]. Currently there are no effective remedial actions available to the industry for smoke impacted grape juice and wine resulting in devastating losses when wildfires occur [2, 3]. Research has shown that during wildfires substantial amounts of volatile phenols (VP's) are released into the air from wood burning through the pyrolysis (thermal decomposition) of lignin. These compounds can be absorbed through the berry skin, where they are quickly glycosylated, potentially as part of the defense mechanism of the plant [4]. Thus, the key volatile phenol smoke exposure marker compounds can be present in the grapes as various glycoconjugates, bound to mono- di- and tri-saccharides.

Research has shown that both the free and bound volatile phenols contribute to smoke taint perception due to bacterial enzymes in saliva that can break down the glycosidic bonds of volatile precursors, releasing smoke taint aroma in the mouth [5, 6]. VP's are naturally present in grape berries and to improve risk assessment the baseline free and bound volatile phenols levels of different winegrapes [7] must be determined. Another important factor to interpret VP's composition of grapes is to know the threshold values of these compounds in different wine matrixes. Prior studies have shown that the wine matrix can have a significant impact on VP expression [5, 8] and that the individual VP's have synergistic interactions with each other. Therefore, the individual odor threshold levels of VP are not a good indicator of potential sensorial impact. In this study, smoke impacted and non-smoke impacted wines of several varieties were used to determine the rejection threshold level of VP's in different wine matrixes. Wines with different levels of VP's were made by serial dilution of the smoke impacted wines with their respective non-impacted wines. Consumer studies were conducted to determine the change in 'liking' for a wine depending on the percentage inclusion of smoke impacted wine.

2 Materials and methods

2.1 Winemaking

Smoke impacted and non-smoked impacted wines were made at the University of California, Davis Teaching and Research Winery using standard experimental winemaking protocols as described in Girardello et al. [9]. Smoke impacted Cabernet Sauvignon (CS), Malbec (MA) and Syrah (SY) wines were made from grapes severely smoke impacted (ST) by the 2020 wildfires in Sonoma County, CA. In 2021, non-smoke impacted wines (NST) were made from grapes from the same vineyard blocks harvested in 2020. The one exception is the Cabernet Sauvignon wines made from Napa Valley County, CA grapes in 2021. Grapes were harvested and divided into non-smoke impacted (21CS_OAK_NST) and smoke impacted (21CS_OAK_ST). The latter were intentionally smoke exposed using a custom-made smoke tent. The grapes were spread on drying tables and intentionally smoked for 2 hours using a Z Grills Wood Pellet Grill Smoker and hickory pellets (Traeger Grills Signature Blend 100% All-Natural Wood Pellets). See Table 1 for the wines' basic chemical composition. Ethanol content % (v/v) was measured with an analyzer (Anton Parr, Ashland, VA, USA), while the pH and titratable acidity (TA) were measured using an Orion 5-star pH meter

(Thermo Fisher Scientific, Waltham, MA, USA) and a Mettler-Toledo DL50 titrator (Mettler-Toledo Inc., Columbus, OH, USA), respectively. Residual sugar (RS) was determined by enzymatic analysis using the Gallery automated analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

Table 1. Wine basic chemical composition. Alcohol percentage (Alc%), titratable acidity in g/L tartaric acid (TA) and residual sugar in g/L glucose (RS).

Wine	Alc %	pH	TA (g/L)	RS (g/L)
20CS_ST	14.1	3.9	5.2	0.4
21CS_NST	14.7	3.8	6.0	0.1
21CS_OAK_ST	15.4	3.5	6.8	0.2
21CS_OAK_NST	15.3	3.5	6.7	0.2
20_MA_ST	15.5	3.6	6.6	0.6
21_MA_NST	15.1	3.3	7.4	0.4
20_SY_ST	14.6	3.4	7.4	0.8
21_SY_NST	13.8	3.6	6.4	0.0

2.2 Volatile phenol analysis

Free and total volatile phenols were analyzed by liquid liquid extraction (LLE) as described in Oberholster et al. [2]. Analyses were performed with an Agilent 6460 gas-chromatography tandem mass spectrometer (GC-MS/MS) (Agilent Technologies, Santa Clara, CA, USA). A J&W DB-WAXetr capillary column was used (30 m x 0.25 mm i.d. x 0.25 µm thickness, Agilent, Santa Clara, CA, USA). Separation conditions were the same as those described in Oberholster et al. [2]. Stable isotopic dilution analysis (SIDA) was used for quantification.

2.3 Sensory analysis

Descriptive Analysis (DA) was performed as described in Oberholster et al. [2] with the following differences: 15 panelists recruited from the University and the city of Davis. The panelists were selected based on their availability, interest and were screened on their sensitivity to smoke using low concentrations of the ashy standard [10]. The study was approved by the Institutional Review Board of the University of California, Davis (IRB ID 1288072-1) and all panelists gave informed written consent. A dextrose solution was used for a rinse in between samples prior to a wait time of 2 min as recommended by Fryer et al. [11]. The reference standard for the retro nasal ashtray sensory attribute were changed to that used by Fryer et al. [10].

A consumer study was performed on wines created by the serial dilution of smoke-impacted Sonoma County CS wine with its non-smoke impacted equivalent. Table 2 shows the composition of each wine used. Wines were served in order of increasing smoke impact. RedJade Sensory Software (RedJade Sensory Solutions, LLC) was used to capture the data. The CS from Sonoma County were evaluated by an expert panel (wine professionals). The expert panel consisted of 62 participants. Consumers first rated each sample based on liking (a 9-point hedonic scale), Just About Right (JAR) and Check-All-That-Apply (CATA) of the sensory attributes identified for the base wines during descriptive analysis.

Table 2. Serial dilution of smoke impacted wines ($p < 0.05$).

Wine	% Smoke impacted wine used	Mean 'liking' score
CS_A	0.00	4.32a
CS_B	1.56	4.27ab
CS_C	3.12	4.42a
CS_D	6.25	3.84b
CS_E	12.50	3.24c
CS_F	25.00	2.47d

Quantitative analysis of GC-MS data was conducted using the Mass Hunter Workstation software suite (version B.09.00, Agilent Technologies, Santa Clara, CA, USA). Statistical analyses were performed using XLSTAT (2019, Addinsoft, New York, NY, USA). All chemical and sensory data were analyzed for statistical significance using multivariate analysis of variance (MANOVA) for the overall main treatment effect. If significant, univariate analyses of variance (ANOVA) measuring the effects of treatment and replicate using a pseudo-mixed-model test were used for all chemical data. ANOVA employing the effects of judge, treatment, and replicate with a pseudo-mixed model was used for the DA. Fisher's least significant differences (LSD) were calculated among univariate mean values to assess significant differences. For the DA data, treatments were compared graphically using principal component analysis (PCA) on the mean data. The chemical and descriptive sensory data were related to one another using multiple factor analysis (MFA). Significant differences were assessed on a 5% significance level ($p < 0.05$). Consumer study data was analyzed using R, Version 4.2.0, "Vigorous Calisthenics" (R Core Team, 2022) and R Studio, Version 2022.02.3. Correspondence analysis in the form of an External preference map which relates CATA results to liking scores, and Penalty Lift analysis to determine quality ratings to CATA results were generated [12].

3 Result and Discussion

In Table 3, the total volatile phenol composition of the different wines evaluated are shown. There is a clear difference between smoke impacted and not impacted wines. Smoke exposure resulted in an increase in all volatile phenols analyzed irrespective of the source of

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smoke (hickory pellet smoke or wildfire smoke). There is also clearly a large varietal impact. Previous research from Australia has shown that Syrah grapes and wines naturally have much higher volatile phenol content then other varieties studied [13]. Figure 1 shows the DA biplot where the first two dimensions explains respectively, 83.3 and 7.1% of the variance. The wines are separated mostly in the first dimension with smoke impacted wines on the rights and non-smoke impacted wines on the left. Smoke impacted wines were correlated with 'sweet BBQ', Liquid Smoke', Cigarette Smoke', 'Ashy' and 'Tar' aromas.

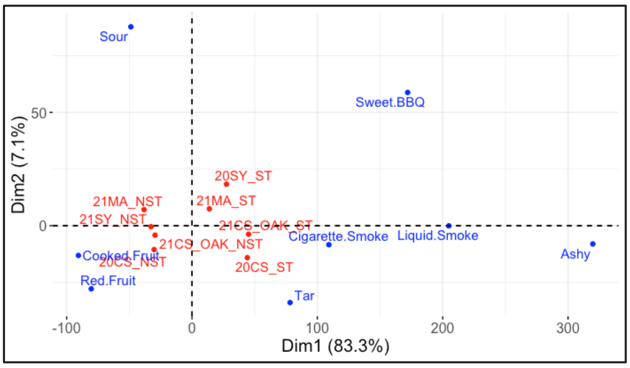
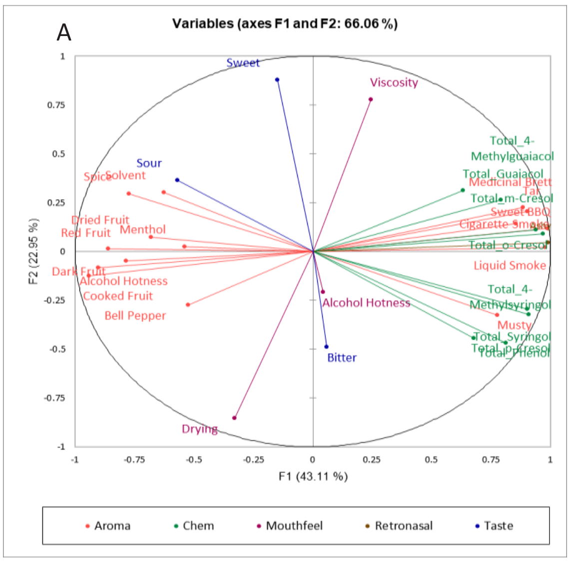


Figure 1. Descriptive analysis biplot of smoke impacted and non-impacted wines showing the eight most prominent attributes.

A MFA was carried out to evaluate the correlations between volatile phenol composition and wine sensory properties (Fig. 2A). The first two dimensions (Factor (F) 1 and 2) described 66.1% of the variability. F1 describes 43.1% of the variance and discriminates wines based on aroma attributes and all the volatile phenols analyzed. F2 described 23.0% of the variance and discriminates wines based on taste and mouthfeel attributes. All aroma attributes related to smoke taint were highly correlated with the volatile phenols analyzed. The score plot (Fig. 1B) indicates that both panelists and instrumental analysis could distinguish among wines based on their smoke impact. It is however important to note that all the smoke impacted wines were heavily impacted by either intentional heavy smoking of 2 hours or by heavy smoke due to large wildfires in close proximity.



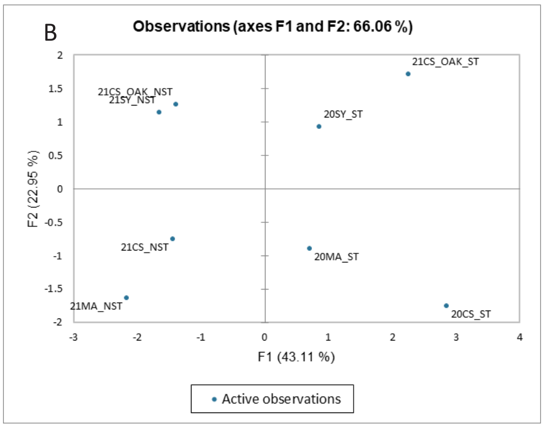


Figure 2. Multi Factor Analysis (MFA) loadings plot (A) which displays the total volatile phenol profiles and sensory attributes and a score plot (B) of the smoke impacted and non-impacted wines.

In a next step the 20CS_ST and 21CS_NST wines were used to create wines that were sequentially less smoke impacted by a process of serial dilution (see Table 2). These wines were rated for overall liking by an expert panel. Liking scores for the CS wines are presented in Table 2. For this particular wine matrix, liking significantly decreased when more than 6.25% of smoke impacted wines were included into the blend. The expert panel were asked to check all the sensory attributes that apply for a specific wine based on the sensory attributes determined using descriptive analysis. Figure 3 shows the CATA score plot of only the significant sensory attributes. The first and second dimension describe respectively 76.0 and 12.7% of the variance. Wines were separated on the first dimension based on fruit, spice, and smoke-related aromas. A decrease in 'liking' was correlated with increasing aromas of barbeque (BBQ), ashy aftertaste and liquid and cigarette smoke. This is also seen in the Penalty Lift Analysis (Fig. 4) where attributes such as red fruit, dark fruit, dried fruit, and baking spice contributed positively towards the overall liking score of the wine. Conversely, liquid smoke, ashy aftertaste, and medicinal & Brett were negative contributors towards overall liking. The consumer study indicated the range where this specific wine may be rejected based on smoke-related sensory attributes.

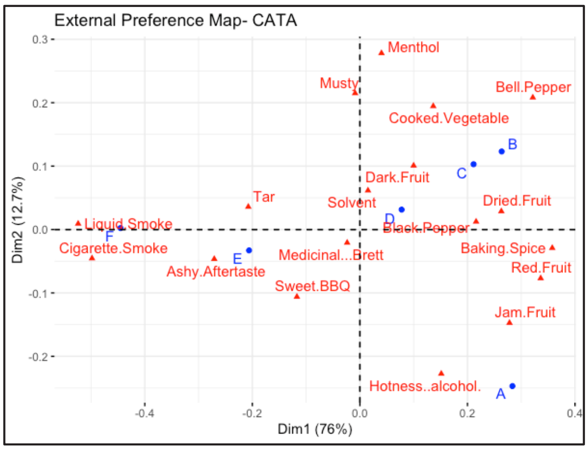


Figure 3. Check-All-That-Apply (CATA) score plot of CS wines containing different amount of smoke impacted wine.

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Table 3. Total volatile phenol composition (μg/L) of wines determined by acid hydrolysis (*n* = 3). 4-MG and 4-MS are 4-methylguaiacol and 4-methylsyringol respectively.

Wine	Guaiacol	4-MG	o-Cresol	Phenol	p-Cresol	m-Cresol	Syringol	4-MS
20CS_ST	84.38±1.04	19.66±1.01	33.42±1.50	112.16±4.06	33.45±1.75	47.76±2.54	415.38±3.40	415.38±0.56
21CS_NST	6.60±0.73	1.02±0.15	2.56±0.29	28.45±5.19	4.45±0.50	3.52±0.32	22.76±1.02	0.35±0.06
21CS_OAK_ST	96.80±1.67	53.26±2.64	39.28±2.11	50.03±3.74	5.00±0.72	65.36±4.36	181.27±02.21	88.64±0.59
21CS_OAK_NST	6.98±0.45	1.07±0.13	2.98±0.23	27.21±3.70	4.49±0.40	4.20±0.25	20.62±0.23	0.53±0.07
20_MA_ST	88.77±0.75	37.92±0.23	21.45±0.44	63.32±0.76	25.42±0.21	29.30±0.49	153.57±2.09	54.85±0.77
21_MA_NST	10.79±0.58	2.79±0.17	3.50±0.26	41.72±5.65	6.76±0.55	6.45±0.36	26.52±0.39	0.62±0.01
20_SY_ST	171.54±9.79	34.70±3.35	21.41±1.71	62.59±3.35	25.28±2.78	28.21±2.42	148.29±0.22	60.50±0.18
21_SY_NST	82.28±1.95	2.49±0.15	6.87±0.51	32.03±3.65	4.82±0.45	4.91±0.15	20.35±0.14	0.70±0.03

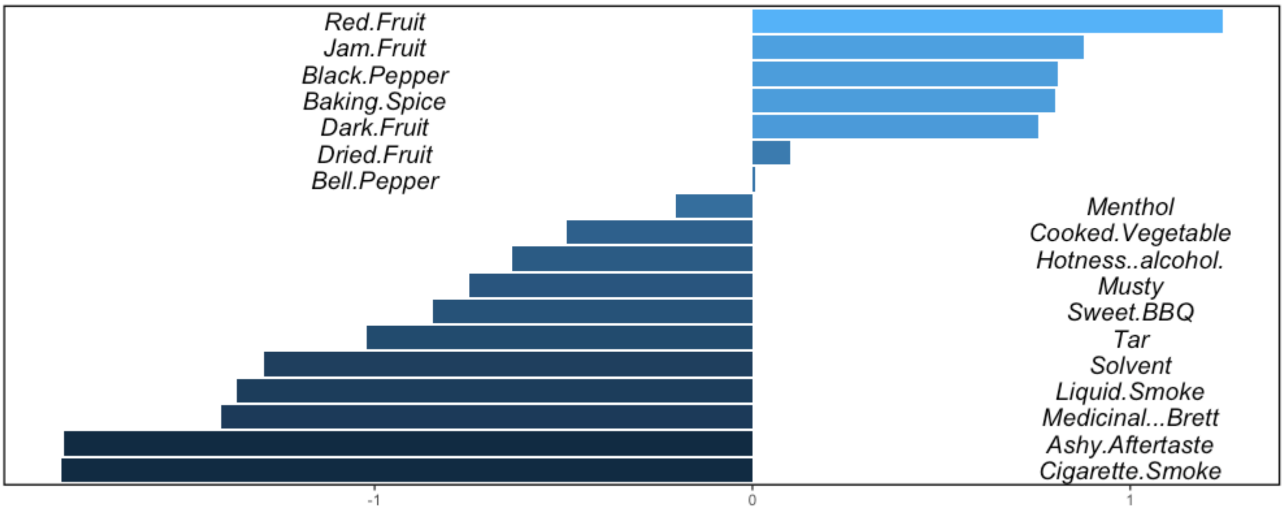

Figure 4. Penalty Lift Analysis relating CATA attributes to the Liking Scores of the CS Wines.

4 Conclusion

Both sensory and instrumental analysis could distinguish among smoke impacted and non-impacted wines. The measured smoke marker compounds (volatile phenols) correlated strongly with smoke-related sensory attributes. Initial consumer studies using an expert panel indicated that a decrease in liking was correlated with smoke-related attributes such barbeque, liquid and cigarette smoke, as well as the retro nasal ashy character. Additionally, linking 'liking' to wine smoke marker compound composition, can determine the odor and rejection threshold levels of these compounds in different wine matrixes.

In a next step difference testing will be used to determine more precisely the rejection threshold for this specific wine matrix.

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