EVALUATION OF VINEYARDS, FRUIT AND WINE AFFECTED BY WILD FIRE SMOKE

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Abstract:

Context and purpose of study - Wineries may randomly reject fruit from vineyards near wild fires exposed to smoke. It is difficult to determine if fruit has been compromised in quality when exposed to smoke, and whether or not smoke taint flavors will result when fruit is fermented into wine. Phenolic smoke compounds bind with sugars in the fruit with enzymes (glycosyltransferases) and are then hydrolyzed during maturation, wine making and even in a taster's mouth. Testing the fruit for volatile phenols and glycosides is both expensive and not completely predictive as standards are not well defined for damage based on smoke chemical content. Micro-vinification even with partially ripened fruit is an inexpensive and fairly accurate method to quickly determine if fruit has a potential smoke taint problem. Wines can then be tasted for the presence of off flavors. Developing standards based on volatile phenolic and glycocide concentrations to predict whether fruit is affected by smoke and how wine will taste when vinified would be very helpful for accepting or rejecting fruit from affected areas.

Materials and methods - Following wild fire smoke exposure, fruit was sampled and micro-vinified during veraison and again 2 weeks before harvest from 13 Cabernet sauvignon vineyards in a transect 25 km across Lake County, California. A control vineyard unexposed to wildfire smoke was sampled outside of the area. Sub samples from each vineyard were analyzed immediately for guaiacol and 4-methyl guaiacol. 19 liter wine lots were then microvinified, stabilized and bottled for each vineyard for both sampling dates. The wine was analyzed for volatile phenols and glycoside compounds (guaiacol and 4-methyl guaiacol, methyl cresol, 4-methyl syringol, o-cresol, p-cresol, syringol, syringol gentiobioside, methyl syringol gentiobioside, phenol rutinoside, cresol rutinoside, guiaocol rutinoside and methyl guaiacol rutinoside). A 14 member tasting panel evaluated the wines for smoke flavors. Panel members were able to detect off flavors in both sample sets, and tainted wines were highly correlated with elevated concentrations of volatile phenols and glycosides. GIS data of vineyard proximity to the fire, elevation, temperature and wind direction and speed were used to conduct multivariate analysis of factors affecting wine smoke compound chemicals and flavor impacts on wine.

Results - Not all wines were affected; in this study, 6µ/l guaiacol was the threshold of detection for off flavors in wine by most tasters. Off flavors were much stronger in the wines made from riper fruit, as were the concentration of smoke compounds, by as much as six fold compared to unfermented fruit. Wind direction and speed, proximity to active fires, and temperature are the factors that are most highly correlated to smoke damage to fruit near wildfires. The control wine sample had no off flavors and no volatile phenols were detected. By ontrast, some sites close to the edge of fires and immediately downwind were very heavily affected, and contained high levels of smoke taint compounds. This study will help to better understand when vineyards are most at risk to wild fire smoke damage, and how micro-vinification may be a reliable and quick way to predict fermentation outcomes before harvest in vineyards affected by wildfire smoke.

Keywords: Wild fire smoke, smoke taint in wine, volatile phenols, glycocides , guaiacol, 4-methyl guaiacol

1. Introduction:

The Mendocino Complex Fires burned more than 165,000 hectares between July 27 to October 4, 2018. The fires began 15 km west in Mendocino County, and north east prevailing winds caused the fire to burn rapidly into Lake County, covering the region's 4,000 hectares of vineyards located around the Clear Lake Basin in dense smoke for weeks (Cal Fire Incident Reports). The smoke from the fire greatly affected wine grape and subsequent wine quality in close proximity to burned areas, but not in all cases. It can be difficult to determine if fruit has been compromised in quality when exposed to wild fire smoke, and whether or not smoke taint flavors will result when fermented. Yet some wineries rejected all fruit from the region without explanation.

During forest and brush fires, large volumes of smoke are produced that can travel many miles and settle into valleys and low lying areas. Smoke makes up about 1.5-2% by weight of the material that has burned. Smoke contains particulates (including tar, ash, carbon and partially burnt fuel fragments), and many gases (CO2, CO, N2O, S2O, NH3, CH4, NOx, ozone, and other non-methane hydrocarbons.) Fresh smoke contains volatile phenols that will affect fruit. These chemicals tend to dissipate fairly rapidly in 1-2 hours, and mostly affect vineyards in close proximity to the fire. Smoke that travels long distances often is mostly suspended carbon particulates and is less likely affect fruit and the resulting fermented wine (Krstic, 2007).

Lignin in wood is the primary source of phenolic compounds that cause smoke flavors in wine grapes and wine following pyrolysis. Phenolic compounds associated with smoke include guaiacol and 4-methyl guaiacol. Both are chemicals that we can taste in smoked food flavoring. These compounds can be found in oak barrels during the toasting process. On their own, these two chemicals have flavor profiles described as "bacon, burnt bacon, smoky, leather, spicy, phenolic, and spicy, salami, and smoked salmon" which doesn't sound so bad. The problem is that there are more than 70 other compounds in forest fire smoke that also produce very undesirable flavors and odors that are described as, "like licking an ash tray, burnt garbage, a burnt potato, a campfire that has been drenched with water." Enzymes, called glycosyltransferases (GTs), bind grape sugars to the smoky phenolic volatiles to form glycosides (Kennison et al., 2007). The phenolic forming compounds from smoke concentrate in the skins of the fruit, more than in the pulp and the juice. If you can minimize skin contact to the juice during harvest, you will also minimize the smoke tastes in the wine. These chemicals are then hydrolyzed during maturation, wine making and even in a taster's mouth. Both guaiacol and 4-methylguaiacol are volatile phenols and are detected in the fruit by gas chromatography, so it is possible to sample fruit before harvest to make picking decisions. While these compounds aren't necessarily the sole cause of smoke flavors, they are highly correlated to many other compounds that cause smoke taint, and are easily detected in the lab. There are protocols in place to test fruit before picking, and anything found to have more than 0.5µ/kg guaiacol is considered likely to have smoke flavor problems. Sampling whole berries is recommended, as the skins of the berries have the highest concentration of guaiacol and 4-methylguaiacol compared to juice. Whole berry test results indicate that levels between 0.5µ to 2.0 µ /kg are moderately affected, and will require special handling and treatment in the winery. Levels above 5 µ/kg in the berries are almost certainly going to have major problems when fermented, and may be cause for rejection by the winery, especially for red fruit since winemaking depends on skin contact where the greatest concentration of smoke compounds are found (Herve et al., 2011) Wineries use flash détente, ultra-filtration, reverse osmosis, carbon fining and filtration and other techniques to remove smoke compounds when concentrations are low.

Testing the fruit for volatile phenolics (guaiacol, 4-methyl guaiacol) and glycosides (cresols, syringol) is both expensive and not completely predictive as standards are not well defined for damage based on smoke chemical concentration. Micro-vinification even with partially ripened fruit is an inexpensive and fairly accurate method to quickly determine if fruit has a potential smoke taint problem (AWRI, 2015). The resulting wine samples can then be more accurately assessed for volatile phenols and glycocides since fermentation concentrates these compounds found in the berries. Volatile phenols including guaiacol, methylguaiacol, *o-, m-* and *p*-cresols, syringol and methylsyringol are important wine flavoring components of smoke generated by wildfires and prescribed burnings. These volatile phenols are taken up by the grape berry during a smoke event and metabolized into their various glycosidic forms (glycosides)especially within the skin of the berry. Therefore, the glycosides in berries, juice and wine can be used as smoke exposure markers. These compounds are referred to as "bound smoke compounds" and may be metabolized during fermentation by yeast. Additionally, sensory analysis of sample wines can be extremely effective in identifying fruit that will have problems when processed.

While few vineyards or structures were damaged by the Mendocino Complex fires, many wineries declined to purchase fruit from the area, resulting in a $37 million disruption to the orderly marketing of fruit for processing (Sommerfield, 2018). There were no quality standards that were agreed upon concerning smoke damage to fruit, and many of the wineries' decisions to decline fruit purchases seemed capricious and unreasonable, especially to growers forced to either abandon their crop or look for other market channels to process their fruit. Other wineries purchased fruit at a discount to cover the cost of ameliorating smoke damaged wine.

This research was initiated to help growers and wineries assess how smoke affected vineyards across the Lake County Winegrowing region. These were questions that we hoped to answer:

1. How effective is the analysis of wine grape fruit for predicting concentration of volatile phenols and glycocides in wine?

2. Are micro-vinifications a quick and effective way of testing for potential smoke off-flavors in smoke affected vineyards?

3. What factors during a wild fire and the release of smoke are correlated to smoke flavor compounds in fruit? (Including: Distance to fire, elevation, temperature, wind direction).

2. Materials and Methods

In this study, 20 kg of Cabernet sauvignon fruit was sampled during the fires just post veraison (August 31) and again when fruit was near complete ripeness (September 27) from 13 Cabernet sauvignon vineyards in a transect across Lake County (approximately 25 km long) representing the major growing regions. An additional vineyard was sampled in Napa Valley (80 km distant) and served as a control as it was not inundated by smoke. A 300 gram berry sub sample from each vineyard was analyzed immediately by a commercial lab for guaiacol and 4-methyl guaiacol. Whole berries were finely ground in presence of an internal standard and extracted by Headspace/SPME. Analysis was performed by GC/MS. Calibration was built using berries not exposed to smoke, spiked with known amounts of guaiacol and 4- guaiacol and 4-methylguaiacol.

With the remainder of the fruit, microvinifications were made using Australian Wine Research Institute protocol to produce sound stable uniform wine samples (AWRI, 2015) in 19 liter fermentation vessels, preserved with sulfites and bottled from each vineyard for both sampling dates, 8 750 ml bottles total for each vineyard sampled. Sample wine from each wine lot was then analyzed by a commercial lab for guaiacol and 4-methyl guaiacol in California (analysis as previously described). Wines were analyzed for volatile phenol and glycoside compounds by the Australian Wine Research Institute (guaiacol and 4-methyl guaiacol, methyl cresol, 4-methyl syringol, o-cresol, p-cresol, syringol, syringol gentiobioside, methyl syringol gentiobioside, phenol rutinoside, cresol rutinoside, guiaocol rutinoside and methyl guaiacol rutinoside). The glycosides in the wine sample were analysed using HPLC-MS/MS and quantified based on a calibration curve constructed by syringol gentiobioside (SyGG) and d_3-syringol gentiobioside (d_3-SyGG) as internal standard, thus all glycoside concentrations are expressed as SyGG equivalent (µg/kg for berry and µg/L for juice or wine). d_3-SyGG is added to wine samples, filtered and analyzed.

A 14 member tasting panel of local winegrowing professionals evaluated the wines for smoke flavors on November 27, 2018 in a blind tasting. The wines were presented as a set of 14 wines for each sampling date. Ratings of the wines were made on a 0 to 5 scale with 0=no defects, 1=barely perceptible defects, 2=slight defects, mostly in mouth feel, 3=noticeable defects in mouthfeel and aroma, 4=serious defects in mouth feel and aroma, 5=very bad aroma, would rather not taste this wine. Data were tabulated and statistically analyzed for regression analysis.

Environmental data (temperature and prevailing wind speed and direction) were collected from weather stations (n = 77) in Lake and Napa Counties near the locations of study vineyards (n = 28) from 27 July to 12 August 2018. For each weather station a mean value for each variable was determined for the data range. Weather station location and data were imported into ArcGIS Pro (ESRI, Redlands, CA). A spatial interpolation (inverse distance weighted, default settings) was conducted on each environmental variable and resulting raster values were extracted at the location of each study vineyard. Data were imported into RStudio (v. 1.1.463) and merged with chemical analysis data, sensory analysis ratings, elevation and distance to fire perimeter for each vineyard. An initial model was built with sensory analysis ratings (n = 14 vineyards) as the dependent variable and all other variables as independent variables.

3. Results

Both fruit and wine samples showed a wide range of volatile phenol and glycocide concentrations indicating that smoke damage to fruit was not uniform across the vineyards sampled (Figure 1). Guaiacol concentrations ranged from <0.5µ to >8.8µ for berries, and <1.0µ to > 36.1µ for wine. The concentrations of both volatile phenols and glycocides increased as fruit ripened, and also increased in the wine from the later sampling date (Table 1, Table 2).

Tasting panel members were able to detect off flavors in both sample sets of wine, and tainted wines were highly correlated with elevated concentrations of volatile phenols and glycosides. Not all wines were affected. Off flavors were much stronger in the wines made from riper fruit, as were the concentration of smoke compounds, by as much as six fold compared to unfermented fruit. At lower concentrations of guaiacol (< 6 µ/i), panel members often did not taste wines as being seriously affected by smoke. The panel was more in agreement that there was something defective in the wine associated with both taste, off aroma and/or mouthfeel with wine samples having above 10 µ/l guaiacol concentration (Figure 2).

Preliminary correlation analysis of chemical compounds suggested the different volatile phenol and glycocide compounds were highly correlated, therefore only guaiacol was included in the model (Figure 1). A stepwise linear regression was conducted on the sensory analysis model, and indicated the best model fit included only guaiacol as the independent variable ($F_{1, 12}$ = 103.5, p <0.001, adj-R^2 = 0.89). A second model tested the relationship between guaiacol in samples and environmental variables, distance from fire perimeter, and elevation. Guaiacol was log() transformed to fit model assumptions and a stepwise linear regression was conducted. The best fit model included distance from fire perimeter, mean daily temperature, prevailing wind speed, and prevailing wind direction ($F_{4, 23}$ = 8.777, p = 0.0001, adj-R^2 = 0.54). Our wine sample from Napa Valley had little off flavors and no volatile phenols were detected (Table 1). On the other hand, some sites close to the edge of fires and immediately downwind were very heavily affected, and contained high concentrations of smoke compounds.

4. Discussion

Fruit samples are useful for a quick evaluation of whether or not a vineyard's fruit may have the presence of volatile phenols, but micro-vinifications are extremely useful for being able to produce a more accurate analysis of what will happen when fruit is processed into wine. As yeasts and bacteria ferment the must, a more accurate measurement of both volatile phenols and glycoside concentrations can be made in the laboratory from the fermented sample, as more of the volatile phenolic compounds are hydrolyzed from the glycocides. In addition, wines can be evaluated for mouthfeel, aroma and taste. Even when fruit is picked and micro-fermented at low sugars, potential major problems are easily recognized in the wine samples, allowing winemakers to take corrective measures in the processing of fruit when it arrives at the winery to reduce smoke flavor impacts, or reject the fruit out right.

Initial results indicate that not all vineyards were equally affected by smoke. Wind direction and speed, temperature, and vineyard proximity to active fires are the factors that are most highly correlated to smoke damage to fruit. Smoke generated in the first one or two hours is most likely to be damaging, whereas smoke that has traveled some distance and for a longer period of time is more likely to contain suspended particulate matter (less than 10 microns) and less of the volatile phenols and glycocides that can be taken up by fruit. Consequently, even though the vineyard may be enveloped in smoke, little damage is done to the fruit when fires are distant. Some of our Lake County vineyard sites had very low levels of all volatile phenolic compounds and no perceptible smoke flavors in sample wines, even though smoke had settled on them for days.

5. Conclusions

Wineries that decided to reject all fruit from Lake County following the Mendocino Complex Fires probably had no justification for those decisions based on the concentration of volatile phenols and glycosides that we detected in the fruit and wine in our study. Our micro-vinifications and careful lab and sensory analysis showed that there were a wide range of sensory effects of the smoke exposure ranging from imperceptible to severely tainted. Our tasting results indicate that guaiacol concentrations less than 6µ/l in wine are difficult to sense and have a minimal effect on the wine. Microvinifications even on very unripe fruit still can be assessed for smoke compound impact and can be done pre-harvest to help make picking and processing decisions. Since the increase of guaiacol concentration is very highly correlated with the increase of other volatile phenols and glycosides, simple chemical analysis of the micro-vinifications for guaiacol will also aid picking decisions and wine treatment protocol to minimize off-flavors. Finally, the factors that cause vineyards to be affected by smoke include wind direction and speed, heat and distance from the active fire. This study will help to better understand when vineyards are most at risk to wild fire smoke damage, and how microvinification may be a reliable and quick way to predict fermentation outcomes before harvest in vineyards affected by wildfire smoke.

6. Acknowledgements:

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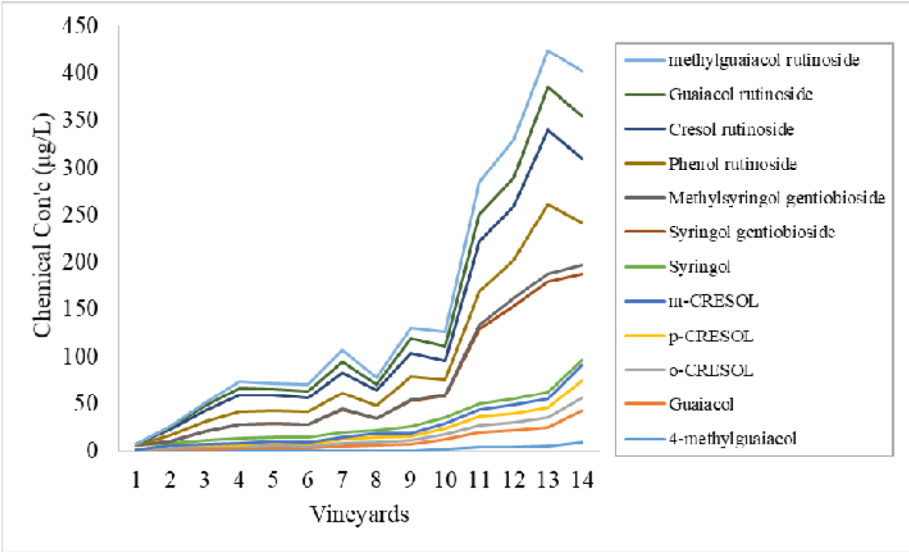

Figure 1: Relative amount of volatile phenols and gylcosides in 14 vineyards in the Lake County area demonstrating that as the concentrations of guaiacol increase, so do all other compounds

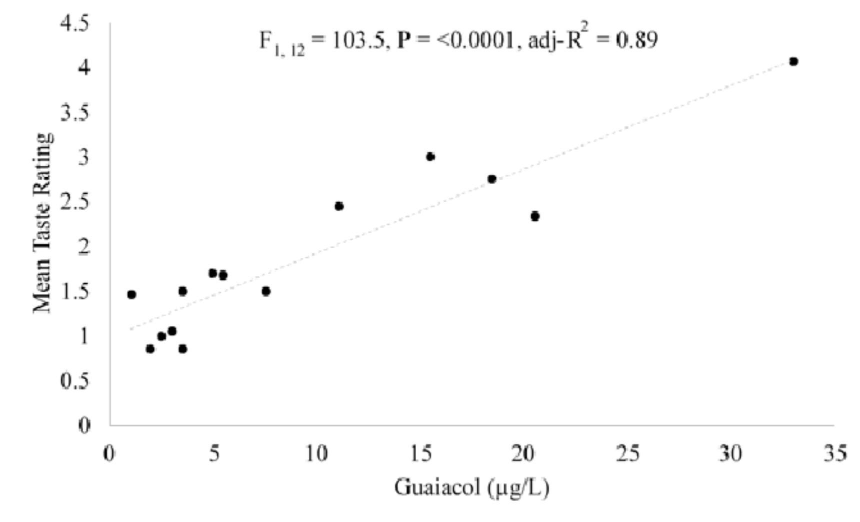

Figure 2. Relationship between guaiacol content and perceived smoke taint for 14 vineyards and 14 tasters, November 27, 2018

Table 1: Guaiacol and 4-methyl guaiacol concentration, berries and wine, first sampling August 21, 2018.

Sample Number	°Brix at Harvest	Berry Guaiacol (µg/kg)	Berry 4-Methyl guaiacol (µg/kg)	Wine Guaiacol (µg/L)	Wine 4-Methylguaiacol/ (µg/L)	Wine Sensory Analysis Rating* (0-5)
1	18.7	0	0	2	<1	0.7
2	15.8	0	0	2	<1	1.0
3	19.3	0	0	3	<1	1.8
4	23.3	0.9	0	7	<1	1.4
5	17.4	0.6	0	4	<1	1.4
6	20.4	1.5	0	9	2	1.5
7	20.2	0	0	1	<1	1.3
8	21.9	7.4	2.3	26	8	3.8
9	19.2	3.2	0.6	17	4	2.5
10	22.3	2.7	0.6	20	5	2.1
11	18.5	0	0	2	<1	0.9
12	18.3	0.6	0	5	<1	1.9
13	19.8	0	0	3	<1	0.9
14	20.6	3.3	0.8	13	4	3.1

Table 2: Guaiacol and 4-methyl guaiacol concentration, berries and wine, second sampling, Sept. 27.

Sample Number	°Brix at Harvest	Berry guaiacol (µg/kg)	Berry 4-methyl guaiacol (µg/kg)	Wine guaiacol (µg/L)	Wine 4-Methyl guaiacol (µg/L)	Wine Sensory Analysis Rating* (0-5)
1	22.7	0.7	0	3	<1	1.0
2	22.7	0.6	0	4	<1	1.0
3	24.0	1.2	0	4	<1	0.8
4	24.7	2.0	0	8	1	1.6
5	24.2	1.8	0	6	1	1.8
6	27.8	3.3	0.7	13	2	2.6
8	24.5	18.0	5.9	40	12	4.3
9	26.2	6.3	1.5	20	4	3.2
10	26.3	5.1	1.1	21	5	2.0
11	21.0	0.3	0	2	<1	0.8
12	20.5	1.9	0	6	1	1.4
13	23.0	0.7	0	4	<1	0.2
14	24.4	4.7	1.2	18	5	2.9

*Sensory analysis ratings: 0=no defects, 1=barely perceptible defects, 2=slight defects, mostly in mouth feel, 3=noticeable defects in mouthfeel and aroma, 4=serious defects in mouth feel and aroma, 5=very bad aroma, would rather not taste this