

Review of smoke taint in wine: smoke-derived volatile phenols and their glycosidic metabolites in grapes and vines as biomarkers for smoke exposure and their role in the sensory perception of smoke taint

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Abstract

In recent years, the exposure of vineyards and grapes to smoke from bushfires and controlled burn events has in some instances resulted in wines described as smoke tainted. Such wines are characterised by undesirable sensory characters described as smoky, burnt, ash, smoky bacon, medicinal and ashtray. This review summarises the knowledge about the composition of smoke from forest and grass fires, describes relationships between smoke exposure of vineyards and smoke taint in wine, and outlines strategies for managing and reducing the risk to producing smoke-affected wines. The sensitivity of grapes and vines at different phenological stages to the uptake of contaminants from smoke, especially smoke-derived volatile phenols, is outlined, and the pathways for entry and metabolic transformation of volatile phenols are discussed. The potential for translocation of phenolic contaminants within the grapevine and the differences in uptake of smoke contaminants of different grape cultivars are also discussed, along with preliminary work on dose/response relationships regarding concentration and duration of exposure and subsequent expression of smoke taint in wine. The chemical basis of smoke taint in wine is described, and the relationship between volatile phenols from combustion of wood/lignin and their glycosides, and sensory panel ratings of smoke attributes in affected wines is discussed. This includes a summary of sensory reconstitution studies and measurement of flavour compounds released from nonvolatile glycosides in mouth and during *in vitro* model experiments, which corroborate the sensory contribution of glycosylated phenolic substances and their role as flavour precursors. Finally, the review also discusses analytical methods used to quantify free volatile phenolic substances and their associated glycosides, biomarkers for identifying smoke exposure of grapes, and strategies for assessing the risk of quality loss post-smoke exposure. Case studies are presented that outline the influence of harvesting and winemaking practices on the expression of smoke taint, and that describe oenological approaches to ameliorate smoke taint in wine.

Keywords: *cresol, glycoconjugates, grapevine, guaiacol, phenolic glycosides, risk management, smoke aroma and flavour, smoke taint, Vitis vinifera L., volatile phenols, wine*

Introduction

The global estimate of land area affected by fire in 2000 was 350 million ha, much of which was forest and woodland located in sub-Saharan Africa (230 million ha), followed at some distance by forest and grass fires in Australia (54.5 million ha) (Joint Research Centre, European Commission 2005). Most of these fires were the result of either a lightning strike (McCarthy et al. 2001) or human-influenced land use (Joint Research Centre, European Commission 2005).

Several studies in Canada (Flannigan and Van Wagner 1991), California (Torn and Fried 1992, Fried et al. 2004) and Australia (Williams et al. 2001, Hennessy et al. 2006, Lucas et al. 2007, Clarke et al. 2013) have all demonstrated that modelling conducted under specific climate change scenarios predicts a high likelihood of increased incidence and severity of wildfires within each country and region studied. The magnitude of the forecast increase is a function of the particular climate change scenario used in the model and the specific vegetation type.

In Canada, modelling under a doubling of ambient carbon dioxide (CO₂) (2× CO₂) climate indicated that a 46% increase in the seasonal severity rating is realistic, together with a similar

increase likely in the area of forest burnt (Flannigan and Van Wagner 1991). In California, Fried et al. (2004) predicted warmer and windier conditions under the 2× CO₂ climate scenario, forecasting fires that burned more intensely and spread faster in most locations. They predicted a 51% increase in the number of escaped fires, those exceeding initial containment limits, in the south San Francisco Bay area and a 125% increase in the Sierra Nevada area. There were no predicted changes for the north coast of California. Changes in area burned by contained fires in these three Californian regions were +41, +41 and -8%, respectively (Fried et al. 2004).

In Australia, approximately 50 million ha of land is burned annually and about 80% of fire-affected areas are in northern savannah regions. Bushfires account for about 10% of the cost of all major natural disasters in Australia, and are associated with the greatest loss of life from natural disasters (Senate Select Committee on Agricultural and Related Industries 2010). Clarke et al. (2013) reported on observed fire weather data in Australia between 1973 and 2010. This was analysed for trends using the McArthur Forest Fire Danger Index (FFDI). Annual cumulative FFDI was observed to increase significantly at 16 of 38 sites, with half of these occurring in significant winegrowing regions

across Australia. None of the sites examined recorded a significant decrease in FFDI. There was an overall increasing trend in the FFDI towards the south-east of Australia, with the largest change likely to occur in the interior of the continent and the smallest near the coastal regions. The total change predicted by aggregating the trends for the regions is typically smaller than the range of interannual variability, which can be quite large depending on the location and season. The combined frequency of days with very high and extreme FFDI ratings is likely to increase by approximately 4–25% by 2020 and between 15 and 70% by 2050 (Hennessy et al. 2006). Modelling under a $2\times$ CO₂ environment in Australia, using the Commonwealth Scientific and Industrial Research Organization (CSIRO) nine-level general circulation model, predicted an increased fire danger risk for all sites from the increase in the number of days of very high and extreme fire danger as a result of changes in maximum temperature (Williams et al. 2001).

Of the three components—fuel, topography and weather—that in combination determine fire behaviour, fuel load is the only one that can be modified by human intervention to moderate the behaviour of wildfires. Reducing the fuel hazard will reduce the overall danger posed by wildfires and increase the potential that a fire may be stopped through natural or artificial means (Senate Select Committee on Agricultural and Related Industries 2010). Hazard reduction burning, or prescribed burning, is being increasingly practised by government agencies around the world. Hazard reduction burning lowers the risk of crown fires developing in medium to tall forests, limits the rate of spread and potential impact of wildfires, and makes fire suppression actions safer, more effective and efficient (Senate Select Committee on Agricultural and Related Industries 2010). At the same time, hazard reduction burns are becoming an increasingly important source of smoke, which can influence human health in sensitive members of the community and impact on surrounding agricultural production land.

The first identification of smoke taint recorded as a problem in the wine industry occurred in Australia in 2003, as a result of the Canberra bushfires, which caused smoke damage to vineyards in north-east Victoria and south-east New South Wales (Høj et al. 2003). In the years since 2003, fires in or near viticultural areas have become a common occurrence and smoke taint has been experienced in wines from other regions of Australia, Canada (Okanagan Valley region, 2003), Greece (Peloponnese region, 2007) and other Mediterranean countries, South Africa (Stellenbosch region, 2009; Western Cape, 2013; Cape Peninsula, 2015) and California (Northern California; Mendocino County, 2008) (Whiting and Krstic 2007, Reynolds 2010).

In Australia, the impact of smoke taint from bushfires, and to a lesser extent controlled burns, can be substantial (Whiting and Krstic 2007). The smoke damage and quality loss from the Canberra bushfires of 2003 was estimated to have cost the north-east Victorian wine industry approximately \$4 million. Bushfires in the Pemberton region of Western Australia were estimated to cost the wine region in excess of \$7.5 million in lost wine revenue from unmarketable grapes in 2004 (Kennison 2009). In 2007, smoke exposure of the north-east Victorian grapegrowing regions effectively resulted in almost no harvest of locally grown grapes, with an estimated loss of 15 000 t of grapes (Kennison 2009). The value of grapes that were at risk of being affected by smoke exposure after the 2006/07 fires in north-east Victoria was estimated at \$15 to 20 million, and the value of the loss of wine not produced in north-east Victoria was much higher at around \$75 to 90 million (Whiting and Krstic 2007). In 2009, the Black Saturday fires in Victoria, Australia,

not only led to the tragic losses of 173 lives, injured 414 people and destroyed approximately 2100 homes, but are estimated to have resulted in approximately \$299 million in lost wine revenue (Brodison 2013).

While wildfires can cause significant economic losses through direct damage to vineyards and wineries, by far the biggest commercial damage is the result of smoke drift into vineyards and exposure of grapes to smoke prior to harvest. This is because wine made from such grapes is often characterised by the presence of objectionable smoky, burnt, burnt rubber, ash, ashy, ashtray, cold ash, smoke salmon, smoked meats, smoked foods, salami, leather, disinfectant/hospital, medicinal, dirty, earthy aromas with 'an excessively drying back-palate and retronasal ash character (Høj et al. 2003, Kennison et al. 2007, 2009, Whiting and Krstic 2007, Hayasaka et al. 2010a, 2013, Parker et al. 2012). Notably, model experiments have established that the intensity of smoke-related sensory attributes in wine is dependent on the timing and duration of grapevine smoke exposure (Kennison et al. 2009).

The purpose of this review was to examine the effect of the exposure of grapes to smoke from forest and grass fires on the composition of grapes and wine, and the sensory properties of wine made from smoke-affected grapes. It also summarises the approaches for assessing a likely impact to grape and wine producers and describes practical methods for modulating and mitigating the expression of smoke taint in finished wine.

Composition of emissions from wood fires

Wildfires, both accidental and planned, occur each year in many parts of the world. These fires can range from small scale to large scale, can burn for hours or weeks, and release substantial quantities of gases, volatile organic compounds (VOCs), particulate matter and smoke into the atmosphere. Notably, smoke emissions from wildfire events and controlled burns from combustion and pyrolysis of lignin, hemicellulose and cellulose are broadly similar to emissions from wood-burning stoves and fireplaces (Andreae and Merlet 2001, Naeher et al. 2007). The composition of wood fire emissions, however, varies as a function of fuel composition and combustion conditions (Lee et al. 2005). Environmental conditions during aerial transport in the atmosphere further affect the VOCs from combustion of biomass and the particle profile in smoke.

The wood combustion process can be summarised briefly as follows (Rogge et al. 1998, Simoneit 2002): when wood is heated, its constituents start to dehydrate, hydrolyse, oxidise, and pyrolyse with increasing temperature, forming combustible volatiles, tarry substances and carbonaceous char. At the ignition temperature of the volatiles and tarry substances, exothermic combustion begins. Resinous compounds and decomposition products of cellulose, hemicelluloses and lignin, together with water vapour are released, then undergo partial to complete combustion in the flaming zone. During the flaming combustion, char formation continues until the combustible volatile flux drops below the minimum level required for the propagation of a flame. During the smouldering process, enough heat is still produced to propagate the charring process as well as the release of additional volatile wood decomposition products.

Smoke is an aerosol of small solid particles and liquid droplets which carry organic components. Wood smoke particles are generally smaller than 1 µm, with a peak in size distribution between 0.15 and 0.4 µm (Kleeman et al. 1999) and particles can be formed both during the initial combustion process and later in the atmosphere. The long-range transport of combustion-derived aerosols which can be attributed to

agricultural burning and bushfires has been demonstrated through the measurement of fine carbon, total soot carbon and excess potassium in particles smaller than 1.7 μm (Andreae 1983).

Atmospheric aerosol formation consists of a complicated set of processes, including the production of nm-sized clusters from gaseous vapours, the growth of these clusters to detectable size and the removal of the growing clusters by coagulation with the pre-existing aerosol particle population (McMurry and Friedlander 1979). Once formed, aerosol particles need to grow to a size larger than 50–100 nm in diameter before they are able to influence the climate, although smaller particles may affect human health and atmospheric chemistry (Kulmala et al. 2012). New particle formation events can be detected at a particle size as small as 1.5 nm using condensation particle counters, air ion spectrometers and differential mobility particle sizers; current measurement techniques for monitoring atmospheric nucleation and for determining the nucleation rate and growth rate under atmospheric conditions have been summarised in a recent review by Kulmala et al. (2012).

VOCs and other organic compounds in emissions from wood fires

The main gases emitted from biomass burning are the key greenhouse gases CO_2 and methane, together with carbon monoxide (CO), sulfur dioxide (SO_2) and nitrogen oxides (NO_x). In wood smoke, VOCs include a broad range of alkanes and alkenes, isoprene and monoterpenes such as α -pinene, halogenated hydrocarbons, aldehydes such as formaldehyde, acetaldehyde and acrolein, alcohols, methoxylated phenols such as guaiacol and syringol from lignin decomposition, benzene and alkyl benzenes, and polycyclic aromatic hydrocarbons [PAHs; Maga (1987), Schauer et al. (2001), Lee et al. (2005), Naeher et al. (2007) and references therein].

Notably, some VOCs are released into the atmosphere by plants, even in the absence of wildfires. For example, eucalypts grow widely in Australia and elsewhere, and for Australia alone their annual release of VOCs into the environment including predominantly isoprene, monoterpenes, sesquiterpenes and aldehydes is estimated at teragram amounts [1 Tg = 10^{12} g, He et al. (2000), Maleknia et al. (2009), Winters et al. (2009)]. While the profile of compounds emitted and their emission rates depend in complex ways upon the ecosystem, health of vegetation, time of year, diurnal variation and a range of other environmental factors, model studies have demonstrated that the concentration of most VOCs in smoke emissions increases significantly in response to temperature increasing from ambient to 80°C (Maleknia et al. 2009). This suggests that some VOCs can easily be released into the atmosphere as a consequence of radiant heat exposure of plants and prior to ignition and combustion of plant biofuels.

Lignin biopolymers represent approximately 20% of the dry mass of wood and are derived from *p*-coumaryl, coniferyl and sinapyl alcohols. The specific composition of lignins differs between soft woods, hard woods and grasses; it also varies between different species and trees of the same species of different age and grown under different conditions (Simoneit 2002). Lignin pyrolysis occurs over a wide temperature range (Maleknia et al. 2009) and leads to a range of phenolic aldehydes and acids, which are predominantly found in smoke particles. Phenol, guaiacol, syringol, various cresols and related substituted phenols are formed as major VOCs from lignin sources. While the profile of individual vanillyl-, syringyl- or coumaryl-type compounds in a smoke VOC or aerosol sample

does not constitute a unique tracer for the original source of biomass that was burned, the relative proportion of such phenolic substances can be used to characterise the nature of the underlying fuel (Simoneit 2002). For example, a detailed study of a broad range of phenolic VOCs in smoke generated from jarrah, karri, marri, pine and oats under controlled conditions demonstrated only a relatively minor difference between the fuel types, with the main exemption being a significantly higher concentration of 4-vinyl guaiacol in smoke from pine and oats. In the same study, the smoke emissions from prescribed burns of marri- and karri-dominated forests as well as from a wild oats pasture had a lignin pyrolysate profile similar to that generated by combustion of the individual fuels during model experiments (Kelly et al. 2012).

Pyrolysis of celluloses in the initial stages involves dehydration, decarboxylation and decarbonylation reactions leading to the release of water, CO and CO_2 . At a temperature above 300°C, depolymerisation reactions of cellulose-based plant materials yield the monosaccharide 1,6-anhydro- β -D-glucopyranose known as levoglucosan (Simoneit et al. 1999). As celluloses and hemicelluloses represent around 60–80% of the dry mass of wood, their thermal decomposition product levoglucosan is a major organic component emitted in high concentration in smoke particulate matter. Hence, levoglucosan can be used as a specific indicator for the presence of emissions in samples of atmospheric particulate matter from the burning of cellulose-containing biomass. It is found at considerable distance from the combustion sources, which enables the tracking of such emissions on a global basis (Simoneit et al. 1999).

At a macro level, particle emissions from combustion of wood are a major source of organic compound emissions into the atmosphere. For example, in the south-east USA, forest fires are estimated to contribute about 20% of the fine particulate matter (particles less than 2.5 μm in diameter: $\text{PM}_{2.5}$) and 6% of VOC emissions, and are considered a main cause of increased $\text{PM}_{2.5}$ levels and visible haze (Lee et al. 2005). In addition to levoglucosan emission from burning of cellulose-containing biomass, organic compounds in aerosols and fine particulate matter from combustion of wood include a broad range of chemicals, including *n*-alkanes, *n*-alkenes, cyclohexylalkanes, alkanals, alkanic acids, alkenic acids, dicarboxylic acids, resin acids, substituted phenols, lignans, alkylated benzenes, substituted benzaldehydes, phytosterols, PAHs and oxygenated PAHs (Rogge et al. 1998, Andreae and Merlet 2001, Schauer et al. 2001, Naeher et al. 2007). Table 1 gives an overview of the distribution of organic compounds between emissions of particulate matter and VOCs in wood smoke.

Notably, the relative abundance of VOCs and other organic compounds in particle emissions from controlled burns and forest fires can be different from residential wood burning emissions. This is because of the mixed fuels, different combustion conditions and extended smouldering that are typical for controlled burns and forest fires (Lee et al. 2005). Differences in sampling methods, analytical techniques and quantification of individual organic compounds may add further to the difficulties with comparing absolute concentration between individual studies. Yet, several source-specific organic compounds (Table 2) have been identified in smoke particles that are valuable as markers to characterise the various fuels used in combustion processes, as well as for differentiation between anthropogenic and biogenic sources of emissions (Simoneit 2002).

In a comprehensive study of the emissions of VOCs in the gas phase and organic compounds in particulate matter from prescribed burns in the south-east USA (Lee et al. 2005), ambient samples were collected at 21 and 26 km downwind

Table 1. Concentration of organic compounds in emissions from wood smoke (adapted from Naehrer et al. 2007).

Compounds	Particulate matter	Volatile organic compounds (VOCs)
Hydrocarbons		
Methane	nd	++
Alkanes (C2-C7)	+	+
Alkenes (C2-C7)	+	++
Alkanols	++	++
Aldehydes and ketones	Reported as VOC	++
Carboxylic acids	+++	+
Carbohydrate derivatives		
Levoglucosan	+++	nd
Aromatic compounds		
Polycyclic aromatic hydrocarbons	+++	+
Guaiacol, other methoxylated phenols	+	++
Other substituted aromatic compounds	+++	++
Other compounds		
Resin acids and terpenoids	+++	+
Phytosteroids	+	nd

+, <1000 mg/kg wood burned; ++, 1000–10 000 mg/kg wood burned; +++, >10 000 mg/kg wood burned; nd, not detected.

Table 2. Markers for fuel source in emissions of particulate matter from smoke (adapted from Simoneit 2002).

Compounds	Fuel source
Monosaccharides	
Levoglucosan	Cellulose
Methoxyphenols	
Vanillin, vanillic acid	Conifers
Syringaldehyde, syringic acid	Angiosperms
<i>p</i> -Hydroxybenzaldehyde, <i>p</i> -hydroxybenzoic acid	Gramineae
Diterpenoids	
Abietic, pimaric, <i>iso</i> -Pimaric acid	Conifers
Dehydroabietic acid	Conifers
Pimanthrene, retene	Conifers
Triterpenoids	
α -Amyrin, β -amyrin, lupeol	Angiosperms
Phytosterols	
β -Sitosterol, stigmasterol campesterol	All gramineae

from the prescribed burn sites. Average particle-phase emissions (PM_{2.5}) were quantified at 1.81 mg/m³. The fine particles contained (by % mass of PM_{2.5}) organic carbon (OC) (60%), elemental carbon (4%), potassium (0.6%), acetate (0.5%), chloride (0.5%), formate (0.4%), nitrate (0.4%), sulfate (0.2%) and ammonium (0.1%) as the most abundant ionic species among the particle-phase emissions after subtracting ambient background levels. A total of 176 mg of organic compounds could be identified per gram of OC in the fine particles, with levoglucosan from the pyrolysis of cellulose being the dominant compound among the identified organic compounds in the particles (95 mg/g OC). It was followed by dehydroabietic acid (33 mg/g OC) and other resin acids that are typical products of the pyrolysis of conifers such as pine, which was the main fuel in this study, plus large-chain alkanolic (27 mg/g OC) and alkenoic acids (5 mg/g OC). Small amounts of alkanes (2.4 mg/g OC) were also detected in the fine particles, and total PAH emissions were 1.5 mg/g OC, with retene as the major compound (0.35 mg/g OC) in the particles. In the same study, ethane and ethene were the main VOCs in gaseous emissions (Lee et al. 2005); traces of

benzene and a range of alkyl benzenes were quantified among the VOC emissions, but no data were given for methoxy phenols (Lee et al. 2005). Notably, VOC emissions from the smouldering stage of the prescribed burns were generally higher than those from flaming. This observation was much more prominent for aromatic and biogenic compounds, such as benzene, toluene, xylenes, isoprene and pinenes, which play an important role in the atmospheric formation of ozone and secondary organic aerosol (SOA) (Lee et al. 2005).

Atmospheric degradation of VOCs

In the troposphere, VOCs are initially transformed by photolysis at wavelengths >290 nm, reaction with the hydroxyl (OH) radical during daylight hours, reaction with the nitrate (NO₃) radical during evening and night-time hours, reaction with ozone, and in coastal and marine areas by reaction with Cl atoms during daylight hours. Rate constants for the gas-phase reactions of VOCs have been summarised by Atkinson and Arey (2003). From the rate constants it is evident that the tropospheric lifetime for typical VOCs from forest fires for example, isoprene, α -pinene, *o*-cresol and benzene, ranges from 1.4, 2.7 and 3.4 h to 9.5 days, respectively, for reaction with OH radicals assuming a 12-h day length. Through reaction with NO₃ radicals the night-time lifetime of isoprene, α -pinene and *o*-cresol is even shorter and ranges from 2.4, to 5.4 and 48 min, respectively (Atkinson and Arey 2003).

The atmospheric chemical transformation of organic compounds also generates additional particulate matter, SOA, which accounts for a substantial fraction of tropospheric aerosol. The formation of semi-volatile, nonvolatile and high-molecular-mass compounds that make up SOA involves a complex series of reactions including: (i) oxidation reactions of VOCs in the gas phase; (ii) reactions in the particle phase; and (iii) continuous chemical reactions in either phase until SOA is lost by physical deposition or oxidation to CO or CO₂. Together these reactions result in recurrent changes in the composition of SOA over several days (Kroll and Seinfeld 2008). In a comprehensive review Hallquist et al. (2009) summarised the current state of knowledge on the global SOA budget, atmospheric degradation mechanisms for SOA precursors, gas-particle partitioning theory and the analytical techniques used to determine the chemical composition of SOA.

While the initial oxidative reactions of VOCs in the atmosphere are relatively well understood, to date a quantitative and predictive understanding of SOA formation does not exist; this represents a major research challenge. The most commonly studied (and probably most important) mechanism of SOA formation in the atmosphere is the oxidation of VOCs, forming products of lower volatility that subsequently partition into the condensed phase. Laboratory studies indicate that SOA formation is dominated mostly by monoterpenes and aromatic compounds that form aerosols. Models informed by laboratory measurements, however, do not always capture the variability of observed SOA, and often underestimate the yield of SOA compared with what has been observed under atmospheric conditions (Kroll and Seinfeld 2008).

Secondary organic aerosol has been generally considered to be a low-viscosity liquid that equilibrates with the surrounding gases. There is recent evidence, however, for solid or semi-solid phases of SOA, which is important as solid and semi-solid particles will exhibit behaviour different from that of liquid particles (Kidd et al. 2014). For example, in a recent study of the composition of SOA from the ozonolysis of α -pinene it was demonstrated that as the relative humidity at which the SOA is formed increased, there was a concomitant decrease in viscosity, accompanied by an increasing contribution from carboxylic acids and a decreasing contribution from higher molecular-mass products. In contrast, SOA that was formed dry and subsequently humidified remained solid (Kidd et al. 2014).

In another model experiment that used guaiacol as the precursor for SOA in an aerosol smog chamber with simulated sunlight, it was observed that SOA formation from guaiacol was completed after less than 30 min. SOA from guaiacol yielded small particles with a diameter between 40 and 90 nm, and environmental conditions like solar radiation or relative humidity influenced not only physical properties, such as aerosol size distribution and formation yield, but also chemical properties, such as the degree of oxidation and amount and types of functional groups (Ofner et al. 2011).

In summary, a broad range of organic compounds are emitted as VOCs in wood smoke which may cause contamination of vines and grapes, and contribute to the formation of undesirable smoke-taint compounds in wine. Yet VOC profiles in wood smoke vary significantly not only as a function of fuel composition, but also because of combustion conditions and diurnal and environmental conditions during aerial transport in the atmosphere. Considering also that controlled burns and wildfires typically involve mixed fuels and typically have an extended smouldering phase after the flaming period, it appears unlikely that a reliable assessment of the potential contamination and quality risk from smoke exposure of vineyards can be based on source apportionment (i.e. the composition of fuel and smoke at a fire) and wind direction alone. Furthermore, a qualitative and quantitative understanding about aerial transport and risk for contamination of vines is absent as to the relative roles by free VOCs versus compounds transported in liquid aerosols and/or absorbed to dry particles.

Bushfire emissions and their potential to contribute to adverse health effects

It is well established that forest, wildland and agricultural fires emit significant quantities of known health-damaging pollutants. The constituents in smoke from these wildfire events are broadly similar to emissions from wood-burning stoves and fireplaces. Hence, the health impacts of exposures to toxic gases, CO, nitric oxide (NO) and nitrogen dioxide (NO₂), respirable particles and some of the other wood smoke constituents such

as benzene and PAHs have been comprehensively documented (Naecher et al. 2007).

As summarised by Reisen and Brown (2006), many studies have shown that bushfire smoke consistently caused the level of respirable particles in downwind communities to exceed ambient air quality standards, and that this was considered to be the primary factor in the adverse health effects observed from bushfire smoke. While healthy adults quickly recovered from short-term exposure to bushfire smoke, adverse health effects were primarily observed among the susceptible population, which includes children, the elderly, pregnant women and people with asthma, as well as people with pre-existing respiratory and/or cardiovascular disease. The majority of bushfire smoke studies concluded that exposure to particulate matter was the main cause of adverse health effects, largely on the basis that the levels found were much in excess of air quality standards used for urban air pollution. Exposure to toxic gases CO, NO₂, SO₂ or O₃ can also be increased in bushfire smoke, but are not often above standards (Reisen and Brown 2006). Emission of benzene from wildfires and from controlled burns for fuel reduction, environmental and agricultural regeneration has been estimated to contribute 2% to the total emission of benzene in Australia in 2013/14, with motor vehicles and domestic burning of solid fuels as the major sources of benzene, contributing 64 and 14%, respectively (National Pollutant Inventory 2015). Similarly, emission of PAHs [as benzo(a)pyrene] from wildfires and controlled burns for fuel reduction, environmental and agricultural regeneration has been estimated to contribute 0.16% to the total PAH emissions in Australia in 2013/14, with domestic burning of solid fuels and motor vehicles as the major sources, contributing 43 and 25%, respectively (National Pollutant Inventory 2015). Further research is needed to clarify the potential impact on community health of these incremental PAH emissions (Reisen and Brown 2006).

Measurement of firefighters' personal exposure to intense bushfire smoke and the assessment of associated health risks provides further insights into health-damaging air pollutants. Extensive personal exposure studies of forest firefighters in the USA (Reinhardt and Ottmar 2004) and recent studies of the exposure to air pollutants from smoke by Australian firefighters at prescribed burns (Reisen and Brown 2009) conclude that the primary hazardous substances of concern include CO, respirable particles and the irritants formaldehyde and acrolein. In contrast, exposure by firefighters to benzene and toluene is typically well below occupational exposure standards, and the highest benzene concentration typically has been experienced by firefighters working with engines and torches burning petroleum-based fuel. For example, in several prescribed and experimental burns in four Australian States and Territories during 2005 and 2006 the benzene and toluene concentration in bushfire smoke ranged from 0.002 to 0.26 and 0.002 to 0.95 mg/m³, respectively, well below their respective exposure standards of 3.2 and 191 mg/m³ (Reisen and Brown 2009). Similarly, sampling of VOCs in the breathing zone of eight individuals with clip-on vapour monitors during controlled model trials using a smoke chamber demonstrated the presence of *n*-hexane, and benzene, toluene and other alkyl benzenes at a low concentration compared with that of the established Australian occupational standards. For example, the mean toluene concentration was measured at 53.91 mg/m³ with the maximum concentration reaching 103.96 mg/m³, compared with a short-term exposure limit of 565 mg/m³ (De Vos et al. 2009).

In summary, adverse health effects from smoke exposure experienced by the general population or indeed vineyard and

winery workers are primarily a concern for susceptible individuals. The relative contribution of wildfire smoke to emission of known hazardous compounds such as benzene and PAHs is relatively low, although the potential for migration into grapes of pollutants adsorbed onto smoke-derived particles does warrant further investigation. Elevated concentration of the primary hazardous air pollutants in wildfire smoke (CO, respirable particles and formaldehyde) are unlikely to result in changes to grape composition that represent a food safety or quality risk in final wines. As discussed in detail below, however, some VOCs from wildfire smoke and controlled burns can contaminate grapes, causing undesirable flavours, major quality losses and economic losses.

Smoke exposure of grapes and vines, berry composition, and wine composition and sensory properties

Smoking of food, where food is exposed directly or indirectly to smoke from certain hardwoods, is one of the oldest processes for preserving and flavouring of food. Preservation is achieved by controlling water activity via dehydration and by diminishing the number of surface bacteria, yet today smoking is primarily used for sensory purposes. Many attempts have been made to isolate and identify flavour compounds from wood smoke as summarised by Maga (1987), Wittkowski and Baltes (1990) and more recently by Guillen and Manzanos (2002). The total number of aroma compounds in wood smoke has been estimated to exceed 500 (Toth and Wittkowski 1985). Volatile phenols have been the subject of several investigations (Wasserman 1966, Fujimaki et al. 1974), also because their presence is usually associated with the desirable preservation effects from smoking of food (Toth and Wittkowski 1985). Guaiacol (2-methoxyphenol), 4-methylguaiacol and syringol (2,6-dimethoxyphenol) are the most abundant volatile phenols in smoke, have an odour quality described as smoky and have a low sensory threshold indicating that they are likely involved in the overall smoke flavour. Yet, early on it was already recognised that mixing the three phenols in the proportion found in smoke condensate did not provide a complete reconstitution of smoke flavour. This pointed towards a role for additional flavour compounds in the perception of smoky flavours in food (Wasserman 1966, Maga 1987). The complexity with adopting a descriptive language for the sensory evaluation of smoke flavour and developing chemically defined standards for the training of sensory panels have been summarised by Ojeda et al. (2002).

In recent years wine producers in Australia, Canada, South Africa, Greece and California have reported an increasing number of cases of the occurrence of smoke taint in wine (Høj et al. 2003, Sheppard et al. 2009, Chong and Cleary 2012). The taint was observed in some wines made from grapes after vineyards had been exposed to wildfires, forest fires and controlled burns. Negatively affected wine was described as having undesirable smoky, dirty, and burnt aroma attributes and also causing a lingering ash flavour on the palate (Høj et al. 2003).

Model experiments confirmed that smoke exposure of grapes was indeed responsible for causing smoke taint in wine. In the first study, Verdelho grapes were harvested at maturity and whole bunches were exposed to smoke generated by combustion of straw in a metal drum for 1 h (Kennison et al. 2007). Unsmoked grapes served as a control, and wine was made from free-run juice of control and smoke-exposed grapes with and without skins added. Sensory studies (aroma only) established a perceptible difference between smoked and unsmoked wines and wine made from smoked grapes were described as exhibit-

ing smoky, dirty, earthy, burnt and smoked meat characters. In the same sample set, a significant concentration of guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-ethylphenol, eugenol and furfural was quantified by GC-MS analysis in each of the wines from smoked grapes, while these compounds were not detected in the unsmoked wines. A subsequent model study (Kennison et al. 2009) described the application of smoke to field-grown grapevines at different time points between veraison and harvest. Merlot vines were exposed to 30 min of high density smoke from barley straw (PM_{10} 200 $\mu\text{g}/\text{m}^3$) as a single application at one of eight individual time points post-veraison, and one additional treatment also received eight cumulative doses of smoke. In wine made from grapes after repeated smoke exposure, but not in control wines, quantitative descriptive wine aroma analysis identified significantly increased aromas of burnt rubber, smoked meat, leather and disinfectant. These aromas clearly dominated the wine's sensory profile, overpowering any confection and red berry fruits aromas. Smoke-like aromas were also present to various degree in all wines vinified from the single smoke exposure experiment regardless of smoke application timing. An elevated concentration of guaiacol, 4-methylguaiacol, 4-ethylguaiacol and 4-ethylphenol was found by GC-MS analysis in all wines produced from fruit from smoked grapevines, and repeated smoke exposures had a cumulative effect on the concentration of these compounds (Kennison et al. 2009). In an extension to this study, smoke was applied to field-grown Merlot grapevines at 12 stages of vine development over three growing seasons (Kennison et al. 2011). Differences in a vine's sensitivity to smoke taint in wine were observed among the different growth stages. Exposure in the period from shoots at 10 cm to full flowering resulted in only a low level of smoke taint detectable in wine; exposure in the period from pea-sized berries to the onset of veraison led to a variable level of smoke taint, and exposure between 7 days post-veraison and harvest led to a high level of smoke taint in wine. Notably, carry-over of the smoke aroma compounds, guaiacol and 4-methylguaiacol, was not detectable when analysing wine made from unsmoked grapes that had been grown on a vine, which had been exposed to smoke in the previous growing season (Kennison et al. 2011).

Altogether, these model studies established guaiacol, 4-methylguaiacol and related volatile phenols as important indicators of smoke exposure of grapes. Yet it also was observed that the presence of volatile phenols was not always positively related to the smoky sensory attributes observed in wines made from smoke-exposed grapes. For example, smoke-like aromas were demonstrated to be present to various degree in all wines made from the single smoke exposure, model experiment regardless of smoke application timing (Kennison et al. 2009), yet the concentration of guaiacol, 4-methylguaiacol, 4-ethylguaiacol and 4-ethylphenol in all these wines was below the reported aroma threshold of these compounds for red wine, except for guaiacol in one treatment.

In a detailed study, several VOCs including phenol and several guaiacol and syringol derivatives and cresol isomers, which also had been found before in other smoked foods, were identified as major VOCs in smoke from a smouldering controlled burn (Parker et al. 2012). Subsequently, the contribution of these volatile phenols to smoke-related sensory properties of 15 red wine samples made from grapes that had been exposed to wildfires was characterised (Parker et al. 2012). In addition, the best-estimate threshold for the aroma properties of these volatile phenols in red wine was established for *m*-cresol (20 $\mu\text{g}/\text{L}$), guaiacol (23 $\mu\text{g}/\text{L}$), *p*-cresol (64 $\mu\text{g}/\text{L}$) and *o*-cresol (62 $\mu\text{g}/\text{L}$) (Parker et al. 2012).

The guaiacol best-estimate threshold (23 µg/L) was exceeded in only five out of 15 smoke-tainted wine samples, and *m*-cresol was present at a concentration similar to its best-estimate threshold (Parker et al. 2012). This result pointed towards: (i) additive or synergistic effects of a range of volatile phenols; and/or (ii) an involvement of additional flavour compounds in the expression of smoke taint in wine. Subsequent partial least squares (PLS) regression analysis revealed that the most important volatile phenols positively associated with both ashy aftertaste and smoke aroma were guaiacol, 4-methylsyringol, 4-methylguaiacol, phenol and *o*- and *m*-cresol. For the medicinal attribute, all of the volatile phenols were positively associated, and syringol was one of the largest contributors to the predictive model for smoke taint, together with *o*-cresol and 4-methylsyringol. The modelling indicated that the smoke-related sensory attributes were well predicted by the volatile phenol data, with calibration coefficients of determination between measured and predicted values for smoky aroma, medicinal aroma, and ashy aftertaste being 0.83, 0.57, and 0.82, respectively. Given the high sensory threshold of 4-methylsyringol and syringol, these compounds were unlikely to be contributing flavour, although there could be an additive effect, as observed for volatile phenols present at subthreshold concentration in beer (Sterckx et al. 2011). A refined model including only the compounds guaiacol, methylguaiacol, vinylguaiacol, and *o*- and *m*-cresol gave a slightly improved predictive ability, with the two cresols being indicated as particularly important.

For guaiacol only, coefficients of determination for predicted versus measured attributes for smoky aroma, medicinal aroma, and ashy aftertaste were 0.72, 0.45, and 0.49, respectively. The low predictive ability of the guaiacol concentration for the ashy aftertaste attribute demonstrated by Parker et al. (2012) is of particular interest, as this particularly negative sensory attribute of smoke-affected wine is considered to be a distinct difference between oak-matured wines (which typically have guaiacol but do not show an ashy aftertaste) and wines made from grapes exposed to forest-fire smoke. As the best-estimate threshold for the aroma of guaiacol (23 µg/L) was comparable to its flavour threshold of 27 µg/L in wine (Parker et al. 2012), differences between aroma and taste thresholds as had been observed before for many volatile phenols in drinking water (Dietz and Traud 1978) were unlikely to explain the limited impact of free guaiacol on the ashy aftertaste flavour attribute in wine. Further study of the additive effects of the concentration of volatile phenols on ashy aftertaste using a stepwise multiple linear regression approach indicated that the best model for ashy aftertaste included only *m*-cresol and guaiacol (Parker et al. 2012). In summary, these experiments demonstrated that several volatile phenols were present at an elevated concentration in wine made from smoke-affected grapes, with guaiacol being the most abundant aroma compound. Therefore volatile phenols from wood smoke including guaiacol, 4-methylguaiacol, 4-methylsyringol, and *o*-, *p*-, and *m*-cresol can be used as indicators for smoke exposure of grapes (Parker et al. 2013). These compounds have been implicated in smoke aroma in other foods and beverages (Jounela-Eriksson and Lehtonen 1981, Clifford 2000) and are likely to contribute smoky aroma to otherwise unoaked white wine. In red wine, however, their diagnostic value is limited as these volatile phenols can also be released in significant concentration from heavily toasted oak during fermentation and wine ageing (Spillman et al. 2004, Prida and Chatonnet 2010). Guaiacol and the other phenols are commonly found in barrel-aged red wine at a concentration exceeding that detected in smoke-tainted wine and so far have

not been recognised as causing a lingering ashy aftertaste in these oaked wine samples. Together, the limited ability for predicting ashy aftertaste from known volatile phenols, the lack of an obvious relationship between guaiacol and smoke taint, and the absence of smoke taint in barrel-aged red wine point toward the presence of additional aroma or flavour compounds in wine made from smoke-affected grapes which are required for the expression of the ashy aftertaste.

Earlier reports had demonstrated the release of guaiacol by acid hydrolysis of precursors from Merlot juice (Sefton 1998) and from Shiraz grapes (Wirth et al. 2001). Subsequently, the release of a substantial quantity of guaiacol and other volatile phenols during the fermentation of Merlot grapes, following grapevine exposure to smoke in model experiments, was observed (Kennison et al. 2008). While only a trace concentration (≤ 1 µg/L) of guaiacol could be detected in the free-run juice from grapes of smoked vines, and wine made from grapes of unsmoked vines contained a maximum of 4 µg/L guaiacol, 388 µg/L guaiacol was observed in the finished Merlot wine. Furthermore, volatile phenols were released from smoked free-run juice by strong acid hydrolysis (pH 1.0) and enzyme hydrolysis with a β -glucosidase, demonstrating the likely presence of a substantial concentration of phenols as glycoconjugates in these grape samples after model smoke experiments (Kennison et al. 2008). In a separate study of guaiacol in wine made from grapes sourced from vineyards after smoke exposure caused by bushfires but without oak contact, it was demonstrated that the guaiacol concentration increased during 3 years of bottle ageing, presumably due to the hydrolytic degradation of guaiacol precursors (Singh et al. 2011).

The *in vivo* conjugation of guaiacol in grapes could be confirmed following application of a mixture of *d*0- and *d*3-guaiacol to leaves and berries (Hayasaka et al. 2010a). The presence of a range of mono- and disaccharide glycosides from guaiacol and other phenolic substances, such as syringol and *m*-cresol, following grapevine smoke exposure was further corroborated by HPLC-MS/MS analysis of grapes following smoke exposure and their resulting wines (Hayasaka et al. 2010b,c).

The availability of glycoside extracts from grapes and wine, and synthesised glycosides as pure reference compounds, laid the foundation for sensory experiments which initially demonstrated the in-mouth release of free volatiles following tasting of guaiacol β -D-glucoside and *m*-cresol β -D-glucoside in model wine, causing a perception of smoky/ashy flavour in-mouth (Parker et al. 2012). Further sensory investigation established the importance of nonvolatile glycoconjugates of phenols relative to volatile phenols on the in-mouth flavour characteristics of smoke-affected wines (Mayr et al. 2014). A PLS regression analysis of sensory and compositional data from wines made in 2007 and 2009 following significant smoke exposure of vineyards because of bushfires showed that the aroma attributes banded and smoky burnt, and the palate attributes banded, burnt/charred, and ashy aftertaste were associated strongly with most of the volatile phenols and their glycosides, while the burning aftertaste attribute was strongly associated with the alcohol concentration of the wines, and was not related to the smoke-related attributes (Mayr et al. 2014). Regarding the key in-mouth attribute ashy aftertaste, almost all volatile phenols and their glycoside conjugates were important to the model. The analytes with the greatest positive contribution were 4-methylguaiacol, guaiacol, the *o*-, *m*- and *p*-cresols, as well as phenol rutinoside, methylguaiacol rutinoside, guaiacol rutinoside and cresol rutinoside (Mayr et al. 2014). The results of this correlative study confirmed those of the previous work by Parker et al. (2012) that multiple volatile phenols and non-

volatile glycoconjugates were together associated with smoky off-flavour. Finally, descriptive sensory analysis was used to characterise differences in the flavour attributes of a red wine, after addition of volatiles, synthetic glycoconjugates, fractions containing glycoconjugates isolated from smoke-affected grapes, or combinations thereof. The attributes medicinal flavour, smoky flavour and burnt ashy' aftertaste were rated as significantly different across the reconstituted wine samples. Importantly, for the wine with the added glycoside fraction isolated from the smoke-affected grapes there was a perceptible flavour effect, with addition of a low concentration of glycosides resulting in significantly higher rating in medicinal compared with that of the base wine, while addition of a higher concentration of glycosides led to a significantly higher rating in 'smoky' flavour compared with that of the base wine. As expected, combining glycoside samples with volatile phenols in the reconstituted wines resulted in a higher rating in the smoky attributes compared with that of glycoside-containing wines with no volatiles added (Mayr et al. 2014).

In conclusion, monoglucosides and disaccharide glycosides of volatile phenols from bushfire smoke can be hydrolysed in-mouth presumably by the activity of enzymes and/or microorganisms, with a great dependency on the glycoside and the individual taster. The concomitant release of phenolic flavour and off-flavour compounds is greatly affected by pH, alcohol and glucose concentration. Considering the buffering properties of saliva, as well as elevated temperature following ingestion, hydrolysis of glycosides is likely to continue as long as wine is kept in the oral cavity during tasting. The decrease in released aroma compounds following microcidal mouthwash provides further evidence that it is in-mouth bacteria that play a role in the hydrolysis of glycosidic flavour precursors. From reconstitution experiments it is clear that the glycosidically bound volatiles have a direct impact on perceived smoke flavour, including aftertaste. Together with the data from the in vitro experiments it is apparent that the breakdown of glycosides in the mouth, including hydrolysis of disaccharide glycosides, is an important mechanism for flavour release in wine that is responsible for the expression of the ashy aftertaste when smoke-tainted wine is consumed. Notably, the addition of volatile phenols together with their glycoconjugates gave the strongest off-flavour in sensory descriptive analysis experiments, mimicking smoke taint in red wines.

Uptake, translocation, carry-over between growing seasons, phenology, influence of cultivar

Metabolism of exogenous compounds in vines and higher plants

Glycosylation of foreign molecules such as xenobiotic alcohols and phenols is one of the main detoxification mechanisms of higher plants (Korte et al. 2000). Alternatively, during transformation of foreign substances in plant tissues, a hydroxyl derivative is formed as one of the primary metabolites, which is then further subjected to fast glycosylation (Korte et al. 2000). In some cases, glycosylation of phenols has been reported with the formation of di- and triglycosides (Korte et al. 2000). For example, in wheat (*Triticum vulgare*) embryo, a diglycoside (gentiobioside) and triglycoside were formed from exogenous hydroquinone (Harborne 1977).

Uptake and localisation within grapevines

Uptake and transformation studies conducted on hypostomatous leaves of *Acer campestre*, *Malus domestica* and *Vitis vinifera* have demonstrated that both benzene and toluene vapours, structurally similar to volatile phenol compounds

found in smoke, penetrate leaves, but were preferentially absorbed via stomates on the abaxial (bottom) side of the leaf and more actively taken up by younger leaves on a shoot (Ugrekheldze et al. 1997). These experiments were conducted under conditions of high stomatal conductance (high humidity and high light) when stomates are mainly open. Hence three potential pathways for entry of volatile phenols into the vine are possible: (i) directly by passive diffusion via the berry cuticle and epidermis; (ii) via the stomates in the leaves and then translocated to the grapes via the vascular system; or (iii) through uptake via the roots and translocation to the grapes. All these pathways may be operating simultaneously, and various studies have drawn different conclusions as to the relative importance of options (i) and (ii), although entry via roots is unlikely because of the dry climatic conditions typically observed around the timing of forest and bushfire events.

In terms of localisation of compounds in fruit, Høj et al. (2003) examined the influence of various aqueous and organic solvent washing treatments of smoke-affected grapes, including cold water, cold water plus wetting agent, warm water (25°C), cold water plus 5% ethanol, 95% ethanol or hexanol. Results indicated that all of the washing treatments listed earlier did not appear to reduce the concentration of guaiacol or 4-methylguaiacol measured in smoke-exposed berries. Also, the washing solution, while containing particulate matter, contained little or no guaiacol, and washed grapes contained the same concentration of guaiacol as that of unwashed grapes. In these initial studies, it was assumed some of those solvents (95% ethanol and hexanol) removed the waxy cuticle, but it was never confirmed by microscopy or analysis of residues from the evaporated solvents (Whiting and Krstic 2007). Kennison (2009) examined the influence of removing the wax bloom with chloroform, and the influence this has on the rate of guaiacol uptake by postharvest/excised berries. Results clearly demonstrated that removal of the waxy cuticle on berries helped to increase the rate of guaiacol uptake following smoke exposure (Kennison 2009).

Further work was conducted to determine the location of the guaiacol within or on the grape, in order to assist the minimisation of its extraction during processing (Høj et al. 2003). Smoke-affected Merlot grapes were separated into skin and pulp fractions and analysed separately. Guaiacol and 4-methylguaiacol were detected in all of the skin samples, but were not detected in any of the pulp samples (Høj et al. 2003). Also, based on the assumption that ethanol and hexane did remove the wax from the cuticle from the grapes, these results suggest that guaiacol from smoke had permeated into the grape skin, but not into the grape pulp (Høj et al. 2003).

Early research on smoke taint investigated the influence of postharvest smoke exposure, using dry straw as the fuel source for smoke generation, on a parcel of hand-picked Verdelho grapes in a purpose-built smoke house and then compared this with an unsmoked control treatment (Kennison et al. 2007). The wines made from grapes exposed to smoke contained a range of detectable volatile phenols, including guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-ethylphenol, eugenol and furfural, in each of the wines made from smoked grapes (Kennison et al. 2007). This indicated that absorption of volatile phenol compounds via the berry cuticle and epidermis was possible.

In 2007, an experiment was conducted in Pinot Noir, near harvest, to assess whether guaiacol could be transported within the vine from the leaves and shoot to the grapes via the grapevine vascular system (Whiting and Krstic 2007). When dilute aqueous guaiacol solutions (1 and 2%) were applied to either decapitated shoots or leaf flaps, a substantial concentration of

guaiacol was observed in grapes sampled from both guaiacol treatments compared with that of control grapes (Whiting and Krstic 2007). This work indicated that free guaiacol is easily translocated throughout the grapevine.

In related work, following the application of smoke-water preparations (containing approximately 35 mg/L guaiacol and 11 mg/L 4-methylguaiacol) to either bunches or leaves directly, uptake of guaiacol and 4-methylguaiacol was observed only in leaf applications of the smoke-water preparation (Kennison 2009). This indicated that the primary mode of uptake is via the leaf surface followed by translocation to the fruit.

The application of an antitranspirant compound (acrylic polymer) to Chardonnay grapevines prior to smoke exposure was also found to reduce the uptake of smoke-derived guaiacol into grapes by approximately 60% (Kennison 2009). The mode of action for the antitranspirant is to reduce the stomatal conductance, giving further credence to the model of entry via leaves being a significant pathway for smoke volatile phenols to enter grapes. Alternatively, the antitranspirant may act as a protective barrier to reduce the uptake of smoke-derived volatile phenols and damage directly by the fruit (Kennison 2009).

Hayasaka et al. (2010a) used a stable isotope tracer technique to demonstrate the biotransformation of guaiacol into its glycosides in both the leaves and berries of potted Cabernet Sauvignon grapevines. Quantitative analysis demonstrated that the guaiacol conjugates were translocated between leaves and berries, but only to a limited extent, and that they were also present at a low concentration in untreated leaves and berries (Hayasaka et al. 2010a). Given that the guaiacol, however, was applied in an aqueous solution to leaves and fruit, this may have resulted in a response that is different from applying guaiacol as a free VOC, as would occur in a wildfire. The authors also reported that guaiacol conjugates were present in both the skin and the pulp portions of the berry, and appeared to be nonspecifically distributed (Hayasaka et al. 2010a). This suggested that once guaiacol had entered the berry through the skin, glycosylation led to a relatively even distribution of conjugates between skin and pulp (Hayasaka et al. 2010a).

Recent research by Kelly et al. (2012) indicated a negative correlation between vine canopy leaf area and concentration of smoke taint-related phenols in wine. Kelly et al. (2012) concluded that the primary mode of entry of the phenolic VOCs into berries is directly via the berry cuticle rather than via leaves. This research indicated that a dense canopy may provide a shielding effect, possibly through protecting berries from smoke particulate matter. In related research, defoliation of vines prior to smoke exposure resulted in wines with a higher concentration of smoke-derived volatile phenols and associated glycosides compared with that of control treatments. Also, defoliation of grapevines following smoke exposure was shown to reduce the severity of smoke taint in grapes and wine (Ristic et al. 2013). These somewhat contradictory findings appear to indicate that both direct absorption via berries and uptake via leaves may be possible and important to the overall expression of smoke-derived taint in grapes and wine, but could vary depending on the circumstances during smoke exposure.

In research that compared the influence of smoke uptake in both excised or in situ bunches in field-applied smoke experiments, preferential uptake of volatile phenol compounds was observed in the excised bunches in preference to those still attached to the vine (Cain 2012). Also, the ratio of free total volatile phenols to bound volatile phenols was higher in the excised bunches. This indicated that there are potentially multiple locations in the vine where glycosylation of volatile phenol compounds may be occurring.

In related research, the aromatic composition of wines was modified after oak extract applications had been applied as a foliar spray to grapevine canopies in the cultivars Verdejo (Martínez-Gil et al. 2011), Petit Verdot (Martínez-Gil et al. 2012), Syrah and Chardonnay (Martínez-Gil et al. 2013), and Monastrell (Pardo-García et al. 2014). These studies show that changes can occur in the aroma of white and red wine when oak extract is applied at the onset of veraison, suggesting that grapes might store volatile aroma compounds, mainly as non-volatile precursors. In addition, these glycosidically bound aroma precursors have also been shown to break down in wines during wine ageing or storage, similar to the observations observed with the breakdown of glycosidically bound smoke-taint compounds. This research demonstrated the foliar absorption and translocation of oak compounds, as these treatments were applied only in a controlled manner using small applications directly to grapevine leaves (Martínez-Gil et al. 2013, Pardo-García et al. 2014).

In summary, smoke-derived volatile phenols can be absorbed both directly via the berry cuticle and via the leaves and translocated to the fruit. Which of these two pathways is more important remains unknown, and the influence of vine physiology on active uptake and/or on passive transport by diffusion also remains poorly understood. Furthermore, the exact location within the vine of glycosylation of these volatile phenol compounds remains an area requiring additional research. Anecdotal evidence suggests that the ratio of free phenols to their glycosidically bound metabolites can vary markedly, even between samples of the same cultivar and from the same smoke event. This indicates that the glycosylation step might be subject to hitherto unknown regulation and potentially could be manipulated by vineyard management.

Implications of smoke density and duration of exposure

Research has demonstrated that a single heavy smoke exposure [30% obscuration (obs)/m] for 30 min at a sensitive stage of growth (any time from 7 days after veraison to harvest) was sufficient to create smoke-related aromas, flavours and compounds in wine (Kennison et al. 2008). A lower smoke density for shorter periods applied at a sensitive vine growth stage can also result in detectable sensory differences by consumers (Brodison 2013).

Smoke-like aromas and flavours are pronounced in wines produced from grapes exposed to a high smoke density (20% obs/m) for a short duration, and a low smoke density (2.5% obs/m) for a long duration (Brodison 2013). As discussed in later parts of this review, it is also important to note that grape harvesting, handling and winemaking techniques can further influence expression of smoke taint in wine. In another study, the effect of repeated ($\times 8$) smoke applications to the same Merlot vines was investigated throughout the growing season. Sensory and chemical analysis of wines demonstrated that repeated smoke exposure had a cumulative effect on the level of smoke-related compounds and aromas observed in the final wines (Kennison et al. 2008).

Influence of vine phenology on smoke uptake

In initial research conducted by Kennison et al. (2009), smoke was applied to Merlot (30 min single applications) at veraison or 3, 7, 10, 15, 18, 21 or 24 days post-veraison. The results demonstrated that smoke applied at all stages resulted in wine with an elevated concentration of guaiacol, 4-methylguaiacol, 4-ethylguaiacol and 4-ethylphenol and detectable smoke taint via sensory analysis compared with that of control wines. A peak period of vine sensitivity, however, to smoke from 7 days post-veraison onwards was observed (Kennison et al. 2009).

Similar results were obtained with Chardonnay, Pinot Gris and Merlot in the Okanagan wine region of Canada, where vines were exposed to smoke generated from Ponderosa pine for 1 h at various stages of development; a trend of increasing concentration of guaiacol and 4-methylguaiacol was observed in grapes as they matured (Sheppard et al. 2009).

In further research conducted by Kennison et al. (2011), smoke was applied to field-grown Merlot grapevines at various stages of phenology, at modified Eichhorn-Lorenz (E-L) (Coombe 1995) stages 12 (10 cm shoots), 23 (full flowering), 31 (pea-sized berries), 32 (bunch closure), 35(a) (onset of veraison), 35(b) (veraison + 3 days), 35(c) (veraison + 7 days), 35(d) (veraison + 10 days), 36(a) (intermediate TSS), 36 (b) (intermediate TSS + 3 days), 37 (berries not quite ripe) and 38 (harvest). Results over 3 years demonstrated a link between phenology and the intensity of smoke taint in wine and enabled the identification of three periods of differing susceptibility to smoke taint (Kennison et al. 2011). The first period (P1), occurs prior to fruitset, where only a low level of taint in wine is observed following grapevine smoke exposure. The second period (P2) occurs between fruitset and the early stages of veraison, where a moderate level of taint is observed in wine following grapevine smoke exposure. The third and final period (P3) occurs between veraison + 7 days and harvest, where an elevated level of guaiacol and 4-methylguaiacol and intense sensory attributes associated with smoke taint are observed in wines made from fruit smoked during this stage of grapevine growth and development (Kennison et al. 2011). In summary, grapes are particularly sensitive to the uptake of volatile phenols from smoke between veraison and harvest. This timing can result in conflict between public land management agencies wishing to manage their planned burning activities and the local wine industry.

A computer-based software platform, the Smoke Taint Risk calculator (STAR) simulation tool predicts the seasonal vine phenological stage and associated susceptibility of the vine to smoke uptake and the effect on wine (Brodison 2013). The tool has been applied in helping to make prescribed burning decisions with public land management agencies in Western Australia in association with vineyard mapping platforms (Brodison 2013).

Influence on vine physiology and yield components and carry-over between seasons

A short duration of smoke exposure for 1 min has been shown to reduce the stomatal conductance, assimilation and intercellular CO₂ level of the evergreen shrub *Chrysanthemoides monilifera*, with full recovery not achieved for 24 h (Gilbert and Ripley 2002). Kennison et al. (2011) postulated that the approximately 50% reduction observed in vine yield in the year following smoke exposure may be related to the negative impact on the photosynthetic capacity of the grapevine. Smoke exposure was shown to decrease the ability of a grapevine to accumulate sugar in grape berries and produced damage on leaf surfaces, via necrotic lesions (Kennison et al. 2009). The reduction in grapevine yield may therefore be a consequence of the effect that smoke has on the physiological functioning of the vine (Kennison et al. 2011).

Other research, however, has shown little effect on the physiology of grapevines from short-term exposure of leaves to smoke for the grapevine cultivars Cabernet Franc, Cabernet Sauvignon, Chardonnay, Durif, Pinot Noir and Syrah, irrespective of fuel type (Bell et al. 2013). Assimilation, stomatal conductance and transpirational levels in most cultivars had recovered to pre-smoke levels within 48 h of initial smoke

application (Bell et al. 2013). It was also noted that the length of exposure time, concentration of smoke components, vine phenology and the interplay of other plant stresses, such as drought, nutrient limitation, competition for water with other plants and high temperature, may also play an important role in plant recovery after exposure to smoke (Bell et al. 2013), and further studies should take these variables into consideration.

Vines exposed to smoke in 1 year to an extent that resulted in significantly smoke-tainted wines have been shown not to carry over the phenols and their metabolites into the following season, with no taint observed in the subsequent year in absence of further smoke exposure (Kennison et al. 2011, Wilkinson et al. 2012, Brodison 2013).

Influence of grape cultivar on the uptake of volatile phenol compounds from smoke

Differences between grape cultivars in the concentration of volatile phenols in wildfire smoke-exposed fruit have been reported (Whiting and Krstic 2007, Hayasaka et al. 2010c, Dungey et al. 2011, Singh et al. 2012, Ristic and Wilkinson 2013). Whiting and Krstic (2007) reported a higher concentration of guaiacol in Sangiovese grapes and wine made from grapes exposed to bushfire smoke compared with other cultivars such as Merlot and Shiraz. They also reported results from over 450 grape samples analysed for guaiacol, where a similar trend was observed in relation to cultivar sensitivity to smoke taint.

Other anecdotal evidence following the 2009 bushfires in Victoria, Australia also suggests that the intensity of smoke taint detected in wine may be dependent on grape cultivar, with Pinot Noir, Sangiovese, Chardonnay and Cabernet Sauvignon thought to be more susceptible than Shiraz and Merlot (Ristic and Wilkinson 2013). Red wines tend to exhibit a higher intensity of smoke taint, likely because of the fact that they are fermented on skins. Ristic and Wilkinson (2013) reported that Cabernet Sauvignon wines were the most smoke tainted, followed by Pinot Noir, Merlot and Shiraz. In the white wines, Pinot Gris was considered the most affected, followed by Sauvignon Blanc and Chardonnay. This study highlighted the limitation in predicting the sensory impact of smoke exposure based alone on analytical data for grape and wine volatile phenol or guaiacol glycoconjugates (Ristic and Wilkinson 2013).

Some of the differences observed among cultivars may be due to differences in the intensity and duration of smoke exposure as well as the timing of smoke exposure in relation to vine phenology (Kennison et al. 2009). Work conducted by Kelly et al. (2014) demonstrated that when smoke exposure events occurred at a comparable stage of berry development (14 days post-veraison) that the cultivar (Sauvignon Blanc, Chardonnay and Merlot) appeared to have no effect on the accumulation of total glycoconjugated phenols. This work highlighted the importance of standardising smoke exposure conditions in model experiments, including duration, intensity and timing in relation to grape development. It was also suggested that variation in cultivar sensitivity observed in earlier reports may have been a reflection of phenology at the time of exposure and exposure conditions rather than demonstrating inherent cultivar differences (Kelly et al. 2014). It was also clear, however, that cultivar differences could be observed for the concentration of volatile phenols in fruit, in the order of Sauvignon Blanc >> Merlot > Chardonnay (Kelly et al. 2014).

In another study, Brodison (2013) investigated the effect of smoke on other cultivars including Cabernet Sauvignon, Chardonnay and Sauvignon Blanc. It was found that the uptake of smoke-related phenols at development stages varied with cultivar. For example, Cabernet Sauvignon appeared to be more

susceptible to smoke uptake at earlier stages of phenology relative to the work conducted on Merlot (Kennison et al. 2011, Brodison and Ward 2012). The differences observed may be due to several factors, including seasonal weather conditions, vine health or inherent phenotypic traits of Cabernet Sauvignon. Wine grape cultivars can differ anatomically in many aspects, such as berry skin thickness and leaf function including anisohydric versus isohydric stomatal behaviour (Schultz 2003), all of which may affect smoke uptake.

In summary, understanding cultivar differences in relation to the uptake and distribution of smoke taint volatile phenols and their glycoconjugates still requires further investigation. While it is important to ensure comparisons are made under standardised exposure conditions (duration, intensity and phenology), to eliminate confounding factors as outlined by Kelly et al. (2014), it is also important to consider the influence of vine physiology on uptake, metabolism and translocation. Factors influencing stomatal conductance and assimilation may be critical in influencing the absorption and biotransformation of smoke-related compounds into grapevines and the influence of drought and water stress also warrants further investigation.

Assessing the risk of smoke taint in grapes and wine

In 2003, the volatile phenols guaiacol and 4-methylguaiacol were considered the most important volatile compounds contributing to the sensory taint in smoke-affected wines (Høj et al. 2003). Further sensory and chemistry work by Kennison et al. (2007) established that guaiacol and 4-methylguaiacol were the primary volatile phenol compounds linked with smoke taint perception in smoke-affected grapes and wine. In wine, however, guaiacol and 4-methylguaiacol can also originate from oak barrel fermentation and/or barrel maturation, and are typically found in oak-treated wines at a concentration of up to 100 and 20 µg/L, respectively (Pollnitz et al. 2004, Kennison et al. 2009). This makes it problematic to use guaiacol and 4-methylguaiacol as indicators of the potential for smoke taint in wine that has been treated with any oak products.

Between 2003 and 2009, guaiacol and 4-methylguaiacol were routinely used by analytical laboratories to assess the potential risk of grapes and/or wine being smoke tainted after exposure to atmospheric smoke. The volatile phenol content of grapes, however, has proven to be a less reliable indicator of the extent of grapevine exposure to smoke (Hayasaka et al. 2011). The mere presence of guaiacol in grapes does not necessarily indicate the occurrence of smoke taint, as guaiacol has been identified as a natural component of several cultivars of *V. vinifera*, including Merlot, Shiraz, Tempranillo and Grenache (Sefton 1998, Wirth et al. 2001, Lopez et al. 2004, Wilkinson et al. 2012). Further research by Parker et al. (2012) demonstrated that other volatile phenols, *m*-cresol, *p*-cresol and *o*-cresol, are also important compounds contributing to the sensory expression of smoke taint in affected wines. Additional volatile phenols, such as syringol, 4-methylsyringol, 4-vinylguaiacol, 4-ethylguaiacol, 4-allylsyringol, 4-ethylphenol, eugenol, furfural and phenol, have all been found in smoke-affected wines (Kennison et al. 2007, 2009, Hayasaka et al. 2010c). Currently, the routine assessment of the concentration of guaiacol, 4-methylguaiacol, *m*-cresol, *p*-cresol, *o*-cresol, syringol and 4-methylsyringol (Parker et al. 2012) is offered by some analytical laboratories to assess the volatile phenol composition of smoke-affected grapes or wine as a means to assess the risk of potential smoke taint.

As volatile phenols can be present naturally in grapes that have not been exposed to atmospheric smoke, it became necessary to compare potentially affected grape or wine samples with the typical background concentration for each grape cultivar. This provided an approach for assessing the likely risk of smoke taint through identifying grapes that showed compositional differences when compared with grapes from smoke-free growing seasons. In a background level study conducted on Chardonnay, Riesling, Pinot Noir, Cabernet Sauvignon and Shiraz in a nonsmoke year, the typical concentration of guaiacol observed in Shiraz was approximately 3.5 µg/kg, with a much lower concentration in Cabernet Sauvignon and Pinot Noir, followed by an even lower concentration in Chardonnay and Riesling (Herderich 2012). In future research, there are two important aspects to consider when undertaking smoke-taint risk assessment based on volatile phenols and other exposure markers: first, the variation observed in guaiacol and 4-methylguaiacol concentration within a single vineyard can be significant, thus sampling strategies need be optimised (Whiting and Krstic 2007); and second, predicting the sensory impact of smoke taint in wine from compositional data for free phenols in grapes or wine can be problematic (Hayasaka et al. 2011, Ristic and Wilkinson 2013).

Hence, the assessment of the glycoconjugate metabolites of volatile phenols is critical to understanding smoke exposure of grapes and the associated overall risk of smoke taint in wine (Hayasaka et al. 2010c, Parker et al. 2012). As volatile phenols have been shown to accumulate in smoke-affected grapes in glycoconjugate forms, the presence of free volatile phenols at or near background concentration does not ensure that grapes are unaffected by smoke taint (Hayasaka et al. 2010b,c, Dungey et al. 2011, Wilkinson et al. 2012). Indeed, several reports have demonstrated that the concentration of guaiacol and 4-methylguaiacol in grapes can be poorly correlated with measurement of their corresponding glycoconjugates (Singh et al. 2011, Wilkinson et al. 2011). For example, guaiacol and 4-methylguaiacol were not detectable in smoke-affected Grenache and Merlot grapes, a low concentration of free guaiacol was observed in a Shiraz sample accompanied by a high concentration of guaiacol glycoconjugates as well as total bound guaiacol and 4-methylguaiacol, and a high concentration of free guaiacol in Pinot Noir samples corresponded to only a moderate concentration of guaiacol glycoconjugates (Wilkinson et al. 2011). These findings again highlight the potential for grapevine smoke exposure to be considerably underestimated by measurement of free grape guaiacol and 4-methylguaiacol alone, and the need for both free and glycoconjugate forms to be analysed to enhance the reliability of detecting grape and wine contamination with phenols from wood smoke.

While most volatile phenols can be detected as glycosylated metabolites in both non-smoked fruit and smoked fruit, the phenolic glycosides found in smoke-affected grapes and wine are typically present at a significantly elevated concentration compared with that of non-smoked control grapes and wines (Hayasaka et al. 2010c). Smoke exposure can increase the pool of grape glycoconjugated phenols by a factor of more than 14 compared with that of control vines (Kelly et al. 2014). Grape glycoconjugates are mainly present as monoglucosides, gentiobiosides, pentosylglucosides and rutinoides. Monoglucoside conjugates, however, were generally less abundant in smoked grapes than disaccharides in most cultivars (Hayasaka et al. 2010c, 2013, Kelly et al. 2014). These smoke-induced glycosides persist and accumulate in grapes until the time of harvest, allowing them to be correlated with the intensity of smoke exposure. Unlike free guaiacol, the concentration of the

phenolic glycosides is low in unsmoked grapes, and they are easily extracted into wine and can act as a pool of precursors which release volatile phenols during fermentation, wine ageing and storage (Hayasaka et al. 2013).

The identification of a range of mono- and disaccharide metabolites in grapes following exposure to free phenols from smoke, and the availability of analytical methods for the quantification of phenolic glycosides in grape homogenates and wine, provided a significant improvement in the ability to distinguish between nonsmoked (clean) and smoke-exposed samples compared with just examining the pool of volatile phenols (Hayasaka et al. 2013). Analysis of glycosides provided a more robust diagnostic strategy to identify smoke exposure and to assess the likely impact of smoke exposure in grapes and the resulting wines (Hayasaka et al. 2013). It was critical to ensure, however, that background concentration in nonsmoke-affected seasons was established to assess smoke taint in grapes and wine—as was the case for the assessment of the concentration of free volatile phenols in grapes and wine. Where possible, the assessment of both free volatile phenols and their associated glycoconjugates is preferable in completing a full risk assessment of potentially smoke-affected grapes and wine.

In order to better assess risk, grape samples are often fermented on a small scale to facilitate the partial conversion of glycoconjugates into their free volatile forms to enhance the sensory detection of a potentially smoke-tainted wine. Yet a major problem that remains unsolved is the inability to accurately predict the degree of smoke taint in wine from grape or wine compositional data alone (Ristic and Wilkinson 2013). Understanding the interactions between the concentration of individual volatile phenols and their associated glycoconjugates on the detection and sensory perception of smoke taint in wine by tasters remains unresolved, especially at a concentration close to the aroma and flavour detection threshold. This is made more complex by the inherent variation that exists among individual wine tasters, and what an individual might be prepared to tolerate in different wine styles.

Analytical methodologies for measuring smoke taint compounds in grapes and wine

A range of analytical methods is currently employed to determine the concentration of free phenols and phenolic glycosides (Pollnitz et al. 2004, Dungey et al. 2011, Wilkinson et al. 2011, Singh et al. 2012, Allen et al. 2013, Hayasaka et al. 2013). The performance of the key HPLC-MS methods for quantification of a range of phenolic glycosides has been fully validated (Hayasaka et al. 2013), and HPLC-MS and alternative GC-MS methods for the determination of free and glycosidically bound guaiacol and 4-methyl guaiacol have been comprehensively compared (Wilkinson et al. 2011).

As an alternative to methods based on GC-MS and HPLC-MS, the potential of using mid-infrared spectroscopy (MIR) and synchronous two-dimensional MIR spectroscopy was explored for the assessment of smoke-tainted wine (Fudge et al. 2012a, 2013). The ability, however, to correctly classify unsmoked and smoked wines based on a spectral prediction of guaiacol and 4-methyl guaiacol was only 61 and 70%, respectively (Fudge et al. 2012a).

Techniques to reduce smoke-related compounds during processing of grapes and wine

Minimising extraction of smoke-taint compounds out of grapes

Early research had indicated that most of the volatile phenols and, to a lesser extent the glycoconjugated phenols, are located in the skin tissue of smoke-affected berries (Høj et al. 2003,

Hayasaka et al. 2010a). Simos (2008) demonstrated that grape leaves contained a high concentration of guaiacol and 4-methylguaiacol, highlighting the importance of ensuring that leaf material was excluded from grapes prior to processing. Research conducted in Pinot Gris has demonstrated that machine-harvested grapes give a higher concentration of guaiacol and 4-methyl guaiacol in must prior to fermentation than hand-harvested grapes (Whiting and Krstic 2007, Simos 2008). This was a result of the higher fruit maceration and skin extraction achieved through the machine harvesting process. Careful hand harvesting followed by bunch pressing was proposed to minimise the extraction of smoke-taint characters in the first 400 L/t of the pressing fraction (Simos 2008). Increased extraction of guaiacol and 4-methylguaiacol was observed beyond 400 L/t press fractions, when increasing pressure was applied to extract juice or wine from must and grape skins (Whiting and Krstic 2007, Kennison et al. 2008, Simos 2008). Cooler fruit temperature during pressing resulted in a lower concentration of guaiacol and 4-methylguaiacol, with 50% less guaiacol observed in the 0–400 L/t pressing fraction conducted at 10°C compared with the 25°C treatment (Whiting and Krstic 2007, Simos 2008).

The use of enzymes has been shown to increase the conversion of glycoconjugated phenols into their free volatile forms. The addition of a β -glucosidase enzyme to free-run Merlot juice affected by smoke enhanced the release of smoke-derived volatile phenols. This was one of the first pieces of evidence that these compounds were being accumulated in conjugated precursor forms (Kennison et al. 2008). As for other glycoconjugates (Gunata et al. 1988), it is reasonable to assume that enzyme treatment of glycoconjugated phenols favours hydrolysis of the monoglucosides and so far no complete hydrolysis of the diverse range of diglycosides has been reported.

Treatment of affected wines by reverse osmosis

Reverse osmosis and solid phase adsorption proved capable and effective processes for reducing the concentration of smoke-derived volatile phenols and the perception smoke taint in smoke-affected Sauvignon Blanc and Pinot Noir wines (Wilkinson 2009, Fudge et al. 2011). Some limitations, however, were identified: (i) the expected concomitant removal of desirable wine volatiles; and (ii) the potential for smoke taint to slowly return with time, probably due to the hydrolysis of residual glycoconjugate precursors, which were not fully removed during the reverse osmosis treatment process. Compared with the direct addition of the adsorptive resins to the wine, the reverse osmosis improved the selectivity of compounds targeted for removal, with less impact on desirable wine attributes. (Wilkinson 2009, Fudge et al. 2011).

As smoke-affected wine ages, acid hydrolysis of phenolic glycoconjugates has been shown to result in increased concentration of the volatile phenols in those wines (Singh et al. 2011), which might lead to more effective reverse osmosis treatments of older wines. Alternatively, an enzyme treatment could be performed prior to reverse osmosis. The effectiveness of either approach, however, would depend on the initial concentration of phenolic glycoconjugates, their structure, chemical stability and/or susceptibility to enzymatic degradation in wine.

Treatment with commercial fining agents

Initial juice and post-fermentation fining trials on smoke-affected Pinot Gris demonstrated that activated charcoal/carbon was the most effective fining agent (Whiting and Krstic 2007, Simos 2008). The addition of 2.0 and 3.0 g/L activated charcoal

substantially reduced the guaiacol concentration of treated wines by 85 and 97%, respectively (Whiting and Krstic 2007). Other trials with Hydroclair (a gelatine-based product) and polyvinylpyrrolidone indicated that these products did not reduce the concentration of guaiacol or 4-methylguaiacol in wine (Whiting and Krstic 2007). In further research by Fudge et al. (2012b) smoke-affected wines were treated with a range of commercially available fining agents, two of which, an activated carbon (added at 1.0 g/L) and a synthetic mineral (added at 2.0 g/L), were found to appreciably ameliorate the taint level in those wines. The activated carbon treatment reduced the concentration of all volatile phenols in both Cabernet Sauvignon and Merlot wines by 53–71% (Fudge et al. 2012b). The synthetic mineral compound had a greater affinity to syringol than the other phenols, reducing the level of syringol by 50%, but removing only small amounts (around 33%) of guaiacol, 4-methylguaiacol and the cresols (Fudge et al. 2012b). Notably, this work did not examine the effect of fining materials on phenolic glycosides in wine. Co-fining with activated carbon and the synthetic mineral compound resulted in a slight improvement in absorption than fining with activated carbon alone. Similar results, however, could have been achieved through using a higher dose of activated carbon alone (Fudge et al. 2012b). Other commercially available fining agents showed poor specificity towards the smoke-taint compounds in wine. It should be noted that the use of activated carbon on smoke-affected wines at the level required to absorb a significant quantity of volatile phenols will remove other desirable 'quality' compounds from wine, likely making the wine inferior in comparison to a similar wine unaffected by smoke.

The effect of yeast and malolactic bacteria

Selected yeast strains can be used as a tool to modulate the level of smoke-related aroma and flavour in smoke-affected grapes and wine (Ristic et al. 2011). Based on descriptive sensory analysis, the yeast strains most capable of reducing smoke aroma and flavour in Grenache wines, without compromising fruit characters were Australian Wine Research Institute (AWRI) 1503 (giving lowest total glycoconjugates in wine at 264 µg/L), ICV GRE (lowest guaiacol concentration at 5.3 µg/L), AWRI Fusion and SIHA active 3 (Ristic et al. 2011). The most intense smoke-related attributes were perceived in smoked wines made from AWRI 1176 (highest total glycoconjugates in wine after fermentation at 374 µg/L), ICV D254, BDX and S6U (highest guaiacol concentration at 12.9 µg/L) (Ristic et al. 2011). Kelly et al. (2014) demonstrated that malolactic fermentation did not significantly affect the concentration or distribution of volatile and glycoconjugated phenols in Merlot wines.

Oak chips and tannin additions

Sensory results indicate that the addition of oak or tannin additives can reduce the perceived intensity of smoke-taint aroma and flavour in smoke-affected wines, albeit through increasing the complexity of wine, rather than through a reduction in the concentration of smoke-derived volatile phenols (Ristic et al. 2011). It is thought that oak volatiles derived from oak chips or tannin additions may mask the sensory contribution of smoke constituents, such as guaiacol and 4-methylguaiacol (Ristic et al. 2011). As such, these additives offer winemakers potential 'masking' options for consideration when processing smoke-affected grapes and wine.

In summary, following smoke exposure of grapevines, several techniques can be employed in both the vineyard and winery to reduce the concentration of undesirable smoke-derived aromas, flavours and compounds in the final wine.

These are summarised and detailed in Table 3 and are more effective when used in combination rather than alone.

Outlook

The understanding of the consequences of smoke exposure of grapevines and grapes and the potential of wood smoke to negatively influence wine composition and sensory properties has advanced significantly over the past 12 years, since the first reports of smoke taint in wine (Høj et al. 2003). Volatile phenols and their associated grape metabolites, the phenolic glycoconjugates, provide a chemical model for defining smoke taint in wine and for obtaining objective measures to identify grapes that have been exposed to smoke from forest and wild-fires. This has improved the capacity to predict the likely impact of smoke exposure in grapes and wine, has improved decision-making in the context of grape intake and winemaking, and overall reduced the risk of producing smoke-tainted wine that is unfit for sale.

There is a need to expand the current suite of cultivars for which comprehensive baseline data are available on the trace concentration of volatile phenols and their glycosides in grapes with and without evident smoke exposure. Clearly, this would enhance the capacity to accurately diagnose contamination with volatile phenols and their metabolites and highlight potential smoke-taint problems, in particular in the cultivars Sauvignon Blanc, Pinot Gris/Grigio, Semillon, Verdelho, Viognier, Merlot, Grenache, Petit Verdot, Mataro, Sangiovese, Durif, Tempranillo and Nebbiolo. It is also important to understand better in a range of oaked and unoaked winestyles how the concentration of various volatile phenols and associated phenolic glycosides relate to wine sensory expression of smoke-taint aroma and flavour, especially at or near the lower limit of sensory threshold and subthreshold concentration for smoke taint compounds, and how consumers perceive and respond to a low level of smoke taint in wine.

Characterising the airborne transport of organic compounds from wild and forest fires

Recent observation during both a forest fire and planned burn located within close proximity to commercial vineyards have demonstrated a large diurnal variation in smoke particulate matter as measured by nephelometry (Mr Ricky James, pers. comm., 2015). This indicates that factors, such as distance from fire, wind direction and topography, might play a major role in the concentration of smoke observed at a particular location, and at a particular point in time.

Considering that controlled burns and wildfires typically involve mixed fuels and have an extended smouldering phase after the flaming period, a better understanding of the smoke composition from wild and forest fires at the source and in vineyards (as opposed to the smoke composition in model experiments), and of the associated risks for contamination of grapes with compounds linked to smoke taint is required. In this context, the relative roles of free VOCs versus compounds transported in liquid aerosols and/or absorbed to dry fine particles warrant special attention, both at the source and after transport to a vineyard, as this will lead to identifying suitable analytical targets for real-time early warning systems. Ground-based sensing techniques using nephelometers (Brodison 2013), aethalometers (Harrison et al. 2013) or low-cost aerosol sensors (Holstius et al. 2014) are readily available, as are aerial and satellite-based remote sensing platforms. Their adoption, however, requires a robust understanding of where and when smoke composition can be measured to reliably predict the

Table 3. Summary of techniques to reduce smoke-related aromas, flavours and compounds during handling and processing of grapes and wine.

Management option	Details
Hand harvest fruit	Minimise breaking or rupturing of skins as long as possible (Whiting and Krstic 2007, Simos 2008)
Exclude leaf material	Leaf material can contribute smoke-related characteristics when in contact with fruit and juice (Whiting and Krstic 2007, Simos 2008).
Wash grapevines	Canopy leaf plucking followed by high-pressure cold water wash in the vineyard can remove ash (Høj et al. 2003); however, washing the entire canopy (including leaves) can accentuate smoke compounds in fruit (Kennison et al. 2008).
Maintain integrity of harvested fruit	Avoid fruit maceration and skin contact with juice as this can lead to a higher concentration of smoke-related compounds (Whiting and Krstic 2007).
Keep fruit cool	Fruit processed at 10°C had less extraction of smoke-related compounds than fruit processed at 25°C (Whiting and Krstic 2007, Simos 2008).
Whole bunch press	Has been shown to reduce extraction of smoke-derived compounds particularly in white wines (Simos 2008, Ulrich 2009).
Separate press fractions	Ferment free-run juice and press fractions separately. Less extraction of phenolic contaminants from smoke in the first 400 L/t fraction, especially when combined with fruit cooling (Whiting and Krstic 2007, Simos 2008, Ulrich 2009).
Conduct trials with fining agents	Carbon, synthetic mineral, PVPP and isinglass fining have shown variable effectiveness in reducing smoke characteristics but are not selective. Fermentation management requires further consideration after fining (Whiting and Krstic 2007, Simos 2008, Ulrich 2009, Fudge et al. 2012b).
Consider yeast selection	Some yeast strains can alter smoke-related aromas, flavours and chemical composition of wine (Ristic et al. 2011).
Minimise fermentation time on skins	Fermentation that reduces skin contact time can reduce smoke aromas and flavours (Kennison et al. 2008, Simos 2008, Ristic et al. 2011).
Consider addition of oak chips and tannin	Oak chips can reduce intensity of smoke characteristics through increased wine complexity (Ristic et al. 2011).
Reverse osmosis of wine	Reverse osmosis can be effective in smoke reduction; however taint might return in the wine over time (Fudge et al. 2011).
Market for quick sale	Smoke-related characteristics can evolve in bottle as wine ages (Simos 2008, Ulrich 2009, Fudge et al. 2011, Singh et al. 2011).

Table adapted from Brodison (2013). PVPP, polyvinylpolypyrrolidone.

potential for smoke taint in wine from smoke compositional data. In addition, we need to resolve whether free VOCs are the sole (or main source) of sensorially active compounds, or whether indeed aerosols and fine particulate matter carry undesirable contaminants as well.

Uptake and metabolism of xenobiotic organic compounds from wood smoke

A detailed understanding across cultivars and clones of key cultivars of the relative importance of passive diffusion of undesirable contaminants across cuticular waxes and the epidermis into grapes, compared with the role played by active stomatal uptake and subsequent transport, potentially could aid in the long term selection of 'low accumulation' cultivars and clones for regions which are at risk from repeated smoke exposure. Also, the impact of vine stomatal conductance, stomatal behaviour in response to water stress, extended drought conditions, elevated temperature and other factors warrant further investigation. Enhanced knowledge about mode of entry would also allow the targeted evaluation and/or development of surface coatings and antitranspirants for grapes and leaves, which could be included in spraying programs for the provision of short-term protection on a needs basis to vineyards located downwind from wildfires and controlled burns.

In addition to research into uptake of VOCs from smoke, a detailed biochemical characterisation of grapevine glycosyl transferases and glycosidases, and their regulation and

inhibition, could prove valuable for reducing in grapes the concentration of phenolic glycosides that are responsible for the ashy flavour and lingering aftertaste in grapes and wine.

Removal of smoke taint-related VOCs and their glycosides from must and wine

There appears scope for an extended screening of yeast and other biological materials for the presence of glycosidases that have the potential to selectively and efficiently hydrolyse taint-related glycosides, especially disaccharides, in must and wine. Obviously, for application in red winemaking glycosidases would be required that are highly selective and will not affect anthocyanins and colour stability. Similarly, identification of phenoloxidases and other phenol-degrading enzymes with substrate specificity towards free phenols and their glycoconjugates would be valuable. Notably, in white winemaking, a combination of such phenol-degrading oxidative enzymes together with hyperoxidation of must might provide practical approaches for lowering or fully removing phenolic taint compounds prior to fermentation. As an alternative to enzymatic remediation strategies, selective removal of key phenolic contaminants, especially glycosides, via membrane processes, and/or through adsorption to selective fining materials would be the ultimate tool for a winemaker who at the end of fermentation or during ageing of wine experiences the development of undesirable levels of smoke taint.

While the incidence of forest and grass fires is predicted to increase in many parts of the world in the future, there has been a significant body of research into assessing and managing the risk associated with smoke-related taint of wine. As the wine industry adapts to climate change, this will likely result in a change in the mix of cultivars grown in particular regions where there is an elevated risk profile for grass and forest fires. Knowledge of smoke-related taint in grapes and wine, and the associated management of this quality issue have advanced substantially over the past 12 years. Additional research to understand better the fundamentals of this problem will further the development of tailored risk management tools that enhance the resilience of grape and wine producers. These will help with successfully mitigating the quality losses and economic consequences of increasing frequency and severity of smoke from wildfires and fuel reduction burns drifting into vineyards.

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References

- Allen, D., Bui, A.D., Cain, N., Rose, G. and Downey, M. (2013) Analysis of free and bound phenolics in wine and grapes by GC-MS after automated SPE. *Analytical and Bioanalytical Chemistry* **405**, 9869–9877.
- Andreae, M.O. (1983) Soot carbon and excess fine potassium: long-range transport of combustion-derived aerosols. *Science* **220**, 1148–1151.
- Andreae, M.O. and Merlet, P. (2001) Emission of trace gases and aerosols from biomass burning. *Global Biogeochemical Cycles* **15**, 955–966.
- Atkinson, R. and Arey, J. (2003) Atmospheric degradation of volatile organic compounds. *Chemical Reviews* **103**, 4605–4638.
- Bell, T.L., Stephens, S.L. and Moritz, M.A. (2013) Short-term physiological effects of smoke on grapevine leaves. *International Journal of Wildland Fire* **22**, 933–946.
- Brodison, K. (2013) Bulletin 4847: effect of smoke in grape and wine production (Department of Agriculture and Food Western Australian: Perth: WA, Australia). <http://citeserx.ist.psu.edu/viewdoc/download?sessionid=7DCE37912829907FD8A627BFB05F4822?doi=10.1.1.392.6887&rep=rep1&type=pdf> [accessed 11/6/15].
- Brodison, K. and Ward, G. (2012) Completing the smoke effect picture: systems development to reduce the negative effects of smoke on grapes and wine. Final report to the Grape and Wine Research and Development Corporation, Project Number: DAW 0901. http://research.agwa.net.au/completed_projects/completing-the-smoke-effect-picture-systems-development-to-reduce-the-negative-effects-of-smoke-on-grapes-and-wine/.
- Cain, N. (2012) Understanding how smoke compounds make it into the fruit and wine. https://www.awri.com.au/wp-content/uploads/smoke_ncain.pdf [accessed 14/05/15].
- Chong, H.H. and Cleary, M. (2012) Smoke taint aroma assessment in 2008 California grape harvest. Qian, M. and Shellhammer, T.H., eds. *Flavour chemistry of wine and other alcoholic beverages* (American Chemical Society: Washington, DC, USA) pp. 67–79.
- Clarke, H., Lucas, C. and Smith, P. (2013) Changes in Australian fire weather between 1973 and 2010. *International Journal of Climatology* **33**, 931–933.
- Clifford, M.N. (2000) Miscellaneous phenols in foods and beverages – nature, occurrence and dietary burden. *Journal of the Science of Food and Agriculture* **80**, 1126–1137.
- Coombe, B.G. (1995) Adoption of a system for identifying grapevine growth stages. *Australian Journal of Grape and Wine Research* **1**, 104–110.
- De Vos, A.J.B.M., Reisen, F., Cook, A., Devine, B. and Weinstein, P. (2009) Respiratory irritants in Australian bushfire smoke: air toxics sampling in a smoke chamber and during prescribed burns. *Archives of Environmental Contamination and Toxicology* **56**, 380–388.
- Dietz, F. and Traud, J. (1978) Geruchs- und Geschmackschwellenkonzentrationen von Phenolkoerpern. *Gas- und Wasserfach. Wasser, Abwasser* **119**, 318–326.
- Dungey, K.A., Hayasaka, Y. and Wilkinson, K.L. (2011) Quantitative analysis of glycoconjugate precursors of guaiacol in smoke-affected grapes using liquid chromatography-tandem mass spectrometry based stable isotope dilution analysis. *Food Chemistry* **126**, 801–806.
- Flannigan, M.D. and Van Wagner, C.E. (1991) Climate change and wildfire in Canada. *Canadian Journal of Forest Research* **21**, 66–72.
- Fried, J.S., Torn, M.S. and Mills, E. (2004) The impact of climate change on wildfire severity: a regional forecast for Northern California. *Climate Change* **64**, 169–191.
- Fudge, A.L., Ristic, R., Wollan, D. and Wilkinson, K.L. (2011) Amelioration of smoke taint in wine by reverse osmosis and solid phase adsorption. *Australian Journal of Grape and Wine Research* **17**, S41–S48.
- Fudge, A.L., Wilkinson, K.L., Ristic, R. and Cozzolino, D. (2012a) Classification of smoke tainted wines using mid-infrared spectroscopy and chemometrics. *Journal of Agricultural and Food Chemistry* **60**, 52–59.
- Fudge, A.L., Schiettecatte, M., Ristic, R., Hayasaka, Y. and Wilkinson, K.L. (2012b) Amelioration of smoke taint in wine by treatment with commercial fining agents. *Australian Journal of Grape and Wine Research* **18**, 302–307.
- Fudge, A.L., Wilkinson, K.L., Ristic, R. and Cozzolino, D. (2013) Synchronous two-dimensional MIR correlation spectroscopy (2D-COS) as a novel method for screening smoke tainted wine. *Food Chemistry* **139**, 115–119.
- Fujimaki, M., Kim, K. and Kurata, T. (1974) Analysis and comparison of flavor constituents in aqueous smoke condensates from various woods. *Agricultural and Biological Chemistry* **38**, 45–52.
- Gilbert, M.E. and Ripley, B.S. (2002) The effect of smoke on the photosynthetic gas exchange of *Chrysanthemoides monilifera*. *South African Journal of Botany* **68**, 525–531.
- Guillen, M.D. and Manzano, M.J. (2002) Study of the volatile composition of an aqueous oak smoke preparation. *Food Chemistry* **79**, 283–292.
- Gunata, Z., Bitteur, S., Brillouet, J.-M., Bayonove, C. and Cordonnier, R. (1988) Sequential enzymic hydrolysis of potentially aromatic glycosides from grape. *Carbohydrate Research* **184**, 139–149.
- Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.H.F., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R. and Wildt, J. (2009) The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics* **9**, 5155–5236.
- Harborne, J.B. (1977) *Introduction to ecological biochemistry* (Academic Press: London, England) pp. 22–27.
- Harrison, R.M., Beddows, D.C.S., Jones, A.M., Calvo, A., Alves, C. and Pio, C. (2013) An evaluation of some issues regarding the use of aethalometers to measure woodsmoke concentrations. *Atmospheric Environment* **80**, 540–548.
- Hayasaka, Y., Baldock, G.A., Pardon, K.H., Jeffery, D.W. and Herderich, M.J. (2010a) Investigation into the formation of guaiacol conjugates in berries and leaves of grapevine *Vitis vinifera* L. Cv. Cabernet Sauvignon using stable isotope tracers combined with HPLC-MS and MS/MS analysis. *Journal of Agricultural and Food Chemistry* **58**, 2076–2081.
- Hayasaka, Y., Dungey, K.A., Baldock, G.A., Kennison, K.R. and Wilkinson, K.L. (2010b) Identification of a [beta]-d-glucopyranoside precursor to guaiacol in grape juice following grapevine exposure to smoke. *Analytica Chimica Acta* **660**, 143–148.
- Hayasaka, Y., Baldock, G.A., Parker, M., Pardon, K.H., Black, C.A., Herderich, M.J. and Jeffery, D.W. (2010c) Glycosylation of smoke-derived volatile phenols in grapes as a consequence of grapevine exposure to bushfire smoke. *Journal of Agricultural and Food Chemistry* **58**, 10989–10998.
- Hayasaka, Y., Baldock, G., Parker, M., Herderich, M. and Pretorius, I. (2011) Seeing through the haze: the discovery of chemical markers for smoke exposure. *Wine & Viticulture Journal* **26** (5), 26–31.
- Hayasaka, Y., Parker, M., Baldock, G.A., Pardon, K.H., Black, C.A., Jeffery, D.W. and Herderich, M.J. (2013) Assessing the impact of smoke exposure in grapes: development and validation of a HPLC-MS/MS method for the quantitative analysis of smoke derived phenolic glycosides in grapes and wine. *Journal of Agricultural and Food Chemistry* **61**, 25–33.
- He, C.R., Murray, F. and Lyons, T. (2000) Monoterpene and isoprene emissions from 15 Eucalyptus species in Australia. *Atmospheric Environment* **34**, 645–655.

- Hennessy, K., Lucas, C., Nicholls, N., Bathols, J., Suppiah, R. and Ricketts, J. (2006) Climate change impacts on fire-weather in south-east Australia (CSIRO Marine and Atmospheric Research: Aspendale, Vic., Australia). http://www.climatechange.vic.gov.au/_data/assets/pdf_file/0020/73208/Fireweatherclimatechange2005.pdf [accessed 14/05/15].
- Herderich, M. (2012) Advances in analytical procedures to assess the likelihood of smoke taint compounds ending up in final wine (The Australian Wine Research Institute: Urrbrae, SA, Australia). https://www.awri.com.au/wp-content/uploads/smoke_mherderich.pdf [accessed 14/05/15].
- Holstius, D.M., Pillariseti, A., Smith, K.R. and Seto, E. (2014) Field calibrations of a low-cost aerosol sensor at a regulatory monitoring site in California. *Atmospheric Measurement Techniques* **7**, 1121–1131.
- Høj, P., Pretorius, I. and Blair, R.J., eds (2003) The Australian Wine Research Institute annual report (The Australian Wine Research Institute: Urrbrae, SA, Australia).
- Joint Research Centre, European Commission (2005) SAFARI 2000 global burned area map, 1-km, Southern Africa, 2000 (The Oak Ridge National Laboratory Distributed Active Archive Center: Oak Ridge, TN, USA). http://daac.ornl.gov/S2K/guides/spot_veg_burned.html [accessed 14/05/15].
- Jounela-Eriksson, P. and Lehtonen, M. (1981) Phenols in the aroma of distilled beverages. Charalambous, G., ed. *The quality of foods and beverages*, Vol. 1, Chemistry and technology (Academic Press: New York, NY, USA) pp. 167–181.
- Kelly, D., Zerihun, A., Singh, D.P., Vitzthum von Eckstaedt, C., Gibberd, M., Grice, K. and Downey, M. (2012) Exposure of grapes to smoke of vegetation with varying lignin composition and accretion of lignin derived putative smoke taint compounds in wine. *Food Chemistry* **135**, 787–798.
- Kelly, D., Zerihun, A., Hayasaka, Y. and Gibberd, M. (2014) Winemaking practice affects the extraction of smoke-borne phenols from grapes into wines. *Australian Journal of Grape and Wine Research* **20**, 386–393.
- Kennison, K. (2009) Bushfire generated smoke taint in grapes and wine. Final report to Grape and Wine Research and Development Corporation, project number: RD 05/02-3 (Department of Agriculture and Food: Perth, WA, Australia).
- Kennison, K.R., Wilkinson, K.L., Williams, H.G., Smith, J.H. and Gibberd, M.R. (2007) Smoke-derived taint in wine: effect of postharvest smoke exposure of grapes on the chemical composition and sensory characteristics of wine. *Journal of Agricultural and Food Chemistry* **55**, 10897–10901.
- Kennison, K.R., Gibberd, M.R., Pollnitz, A.P. and Wilkinson, K.L. (2008) Smoke-derived taint in wine: the release of smoke-derived volatile phenols during fermentation of Merlot juice following grapevine exposure to smoke. *Journal of Agricultural and Food Chemistry* **56**, 7379–7383.
- Kennison, K.R., Wilkinson, K.L., Pollnitz, A.P., Williams, H.G. and Gibberd, M.R. (2009) Effect of timing and duration of grapevine exposure to smoke on the composition and sensory properties of wine. *Australian Journal of Grape and Wine Research* **15**, 228–237.
- Kennison, K.R., Wilkinson, K.L., Pollnitz, A.P., Williams, H.G. and Gibberd, M.R. (2011) Effect of smoke application to field-grown Merlot grapevines at key phenological growth stages on wine sensory and chemical properties. *Australian Journal of Grape and Wine Research* **17**, S5–S12.
- Kidd, C., Perraud, V., Wingen, L.M. and Finlayson-Pitts, B.J. (2014) Integrating phase and composition of secondary organic aerosol from the ozonolysis of α -pinene. *Proceedings of the National Academy of Sciences of the United States of America* **111**, 7552–7557.
- Kleeman, M.J., Schauer, J.J. and Cass, G.R. (1999) Size and composition distribution of fine particulate matter emitted from wood burning, meat charbroiling, and cigarettes. *Environmental Science and Technology* **33**, 3516–3523.
- Korte, F., Kvesitadze, G., Ugrehelidze, D., Gordeziani, M., Khatisashvili, G., Buadze, O., Zaalishvili, G. and Coulston, F. (2000) Organic toxicants and plants. *Ecotoxicology and Environmental Safety* **47**, 1–26.
- Kroll, J.H. and Seinfeld, J.H. (2008) Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere. *Atmospheric Environment* **42**, 3593–3624.
- Kulmala, M., Petäjä, T., Nieminen, T., Sipilä, M., Manninen, H.E., Lehtipalo, K., Dal Maso, M., Aalto, P.P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K.E.J., Ari Laaksonen, A. and Kerminen, V. (2012) Measurement of the nucleation of atmospheric aerosol particles. *Nature Protocols* **7**, 1651–1667.
- Lee, S., Baumann, K., Schauer, J.J., Sheesley, R.J., Naeher, L.P., Meinardi, S., Blake, D.R., Edgerton, E.S., Russell, A.G. and Clements, M. (2005) Gaseous and particulate emissions from prescribed burning in Georgia. *Environmental Science and Technology* **39**, 9049–9056.
- Lopez, R., Ezpeleta, E., Sanchez, I., Cacho, J. and Ferreira, V. (2004) Analysis of the aroma intensities of volatile compounds released from mild acid hydrolysates of odourless precursors extracted from Tempranillo and Grenache grapes using gas chromatography-olfactometry. *Food Chemistry* **88**, 95–103.
- Lucas, C., Hennessy, K., Mills, G. and Bathols, J. (2007) Bushfire weather in Southeast Australia: recent trends and projected climate change impacts (Bushfire Cooperative Research Centre: East Melbourne, Vic., Australia). <http://www.bushfirecrc.com/publications/citation/bf-1038> [accessed 14/05/15].
- Maga, J.A. (1987) The flavour chemistry of wood smoke. *Food Reviews International* **3**, 139–183.
- Maleknia, S.D., Bell, T.L. and Adams, M.A. (2009) Eucalypt smoke and wildfires: temperature dependent emissions of biogenic volatile organic compounds. *International Journal of Mass Spectrometry* **279**, 126–133.
- Martínez-Gil, A.M., Garde-Cerdán, T., Martínez, L., Alonso, G.L. and Salinas, M.R. (2011) Effect of oak extract application to Verdejo grapevines on grape and wine aroma. *Journal of Agricultural and Food Chemistry* **59**, 3253–3263.
- Martínez-Gil, A.M., Garde-Cerdán, T., Zalacain, A., Pardo-García, A.I. and Salinas, M.R. (2012) Applications of an oak extract on Petit Verdot grapevines. Influence on grape and wine volatile compounds. *Food Chemistry* **132**, 1836–1845.
- Martínez-Gil, A.M., Angenieux, M., Pardo-García, A.I., Alonzo, G.L., Ojeda, H. and Salinas, M.R. (2013) Glycosidic aroma precursors of Syrah and Chardonnay grapes after an oak extract application to the grapevines. *Food Chemistry* **138**, 956–965.
- Mayr, C.M., Parker, P., Baldock, G.A., Black, C.A., Pardon, K.H., Williamson, P.O., Herderich, M.J. and Francis, I.L. (2014) Determination of the importance of in-mouth release of volatile phenol glycoconjugates to the flavor of smoke-tainted wines. *Journal of Agricultural and Food Chemistry* **62**, 2327–2336.
- McCarthy, J.J., Canziani, O.F., Leary, N.A., Dokken, D.J. and White, K.S., eds (2001) *Climate change 2001: impacts, adaptation and vulnerability* (Cambridge University Press: Cambridge, England).
- McMurry, P.H. and Friedlander, S.K. (1979) New particle formation in the presence of aerosol. *Atmospheric Environment* **13**, 1635–1651.
- Naeher, L.P., Brauer, M., Lipsett, M., Zelikoff, J.T., Simpson, C.D., Koenig, J.Q. and Smith, K.R. (2007) *Inhalation Toxicology* **19**, 67–106.
- National Pollutant Inventory (2015) National Pollutant Inventory website (Australian Government: Canberra, ACT, Australia). <http://www.npi.gov.au/substances/substance-list-and-thresholds> [accessed 02/04/15].
- Ofner, J., Kruger, H.-U., Grothe, H., Schmitt-Kopplin, P., Whitmore, K. and Zetzsch, C. (2011) Physico-chemical characterization of SOA derived from catechol and guaiacol – a model substance for the aromatic fraction of atmospheric HULIS. *Atmospheric Chemistry and Physics* **11**, 1–15.
- Ojeda, M., Barcenas, P., Perez-Elortondo, F.J., Albisu, M. and Guillen, M.D. (2002) Chemical references in sensory analysis of smoke flavourings. *Food Chemistry* **78**, 433–442.
- Pardo-García, A.I., Serrano de la Hoz, K., Zalacain, A., Alonso, G.L. and Salinas, M.R. (2014) Effect of vine foliar treatments on the varietal aroma of Monastrell wines. *Food Chemistry* **163**, 258–266.
- Parker, M., Osidacz, P., Baldock, G., Hayasaka, Y., Black, C., Pardon, K., Jeffery, D., Geue, J., Herderich, M. and Francis, I. (2012) Contribution of several volatile phenols and their glycoconjugates to smoke-related sensory properties of red wine. *Journal of Agricultural and Food Chemistry* **60**, 2629–2637.
- Parker, M., Baldock, G., Hayasaka, Y., Mayr, C., Williamson, P., Francis, I.L., Krstic, M., Herderich, M. and Johnson, D. (2013) Seeing through smoke. *Wine & Viticulture Journal* **28**, 42–46.
- Pollnitz, A.P., Pardon, K.H., Sykes, M. and Sefton, M.A. (2004) The effects of sample preparation and gas chromatograph injection techniques on the accuracy of measuring guaiacol, 4-methylguaiacol and other volatile oak compounds in oak extracts by stable isotope dilution analyses. *Journal of Agricultural and Food Chemistry* **52**, 3244–3252.
- Prida, A. and Chatonnet, P. (2010) Impact of oak-derived compounds on the olfactory perception of barrel-aged wines. *American Journal of Enology and Viticulture* **61**, 408–413.
- Reinhardt, T.E. and Ottmar, R.D. (2004) Baseline measurements of smoke exposure among wildland firefighters. *Journal of Occupational and Environmental Hygiene* **1**, 593–606.
- Reisen, F. and Brown, S.K. (2006) Implications for community health from exposure to bushfire air toxics. *Environmental Chemistry* **3**, 235–243.
- Reisen, F. and Brown, S.K. (2009) Australian firefighters' exposure to air toxics during bushfire burns of autumn 2005 and 2006. *Environment International* **35**, 342–352.
- Reynolds, A., ed. (2010) *Managing wine quality*, Vol. 2, Oenology and wine quality (Woodhead Publishing Limited: Cambridge, England).
- Ristic, R. and Wilkinson, K. (2013) Varietal response to smoke exposure. *Wine & Viticulture Journal* **28** (1), 40–41.

- Ristic, R., Osidacz, P., Pinchbeck, K.A., Hayasaka, Y., Fudge, A.L. and Wilkinson, K.L. (2011) The effect of winemaking techniques on the intensity of smoke taint in wine. *Australian Journal of Grape and Wine Research* **17**, 29–40.
- Ristic, R., Pinchbeck, K.A., Fudge, A.L., Hayasaka, Y. and Wilkinson, K.L. (2013) Effect of leaf removal and grapevine smoke exposure on colour, chemical composition and sensory properties of Chardonnay wines. *Australian Journal of Grape and Wine Research* **19**, 230–237.
- Rogge, W.F., Hildemann, L.M., Mazurek, M., Cass, G.R. and Simoneit, B.R.T. (1998) Sources of fine organic aerosol. 9. Pine, oak and synthetic log combustion in residential fireplaces. *Environmental Science and Technology* **32**, 13–22.
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (2001) Measurement of emissions from air pollution sources. 3. C1–C29 organic compounds from fireplace combustion of wood. *Environmental Science and Technology* **35**, 1716–1728.
- Schultz, H.R. (2003) Differences in hydraulic architecture account for near-isohydric and anisohydric behaviour of two field-grown *Vitis vinifera* L. cultivars during drought. *Plant, Cell and Environment* **26**, 1393–1405.
- Sefton, M.A. (1998) Hydrolytically-released volatile secondary metabolites from a juice sample of *Vitis vinifera* grape cvs Merlot and Cabernet Sauvignon. *Australian Journal of Grape and Wine Research* **4**, 30–38.
- Senate Select Committee on Agricultural and Related Industries (2010) The incidence and severity of bushfires across Australia (Parliament of Australia: Canberra, ACT, Australia). http://www.aph.gov.au/Parliamentary_Business/Committees/Senate/Former_Committees/agric/completed_inquiries/2008-10/bushfires/report/index [accessed 04/06/15].
- Sheppard, S.I., Dhesi, M.K. and Eggers, N.J. (2009) Effect of pre- and postveraison smoke exposure on guaiacol and 4-methylguaiacol concentration in mature grapes. *American Journal of Enology and Viticulture* **60**, 98–103.
- Simoneit, B.R.T. (2002) Biomass burning – a review of organic tracers for smoke from incomplete combustion. *Applied Geochemistry* **17**, 129–162.
- Simoneit, B.R.T., Schauer, C.G., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F. and Cass, G.R. (1999) Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmospheric Environment* **33**, 173–182.
- Simos, C. (2008) The implications of smoke taint and management practices. *Australian Viticulture* **Jan/Feb**, 77–80.
- Singh, D.P., Chong, H.H., Pitt, K.M., Cleary, M., Dokoozlian, N.K. and Downey, M.O. (2011) Guaiacol and 4-methylguaiacol accumulate in wines made from smoke-affected fruit because of hydrolysis of their conjugates. *Australian Journal of Grape and Wine Research* **17**, S13–S21.
- Singh, D.P., Zerihun, A., Kelly, D., Cain, N.M., Nankervis, P. and Downey, M.O. (2012) A GC-MS based analytical method for detection of smoke taint associated phenols in smoke affected wines. *Current Bioactive Compounds* **8**, 190–199.
- Spillman, P.J., Sefton, M.A. and Gawel, R. (2004) The effect of oak wood source, location of seasoning and coopering on the composition of volatile compounds in oak-matured wines. *Australian Journal of Grape and Wine Research* **10**, 216–226.
- Sterckx, F.L., Missiaen, J., Saison, D. and Delvaux, F.R. (2011) Contribution of monophenols to beer flavour based on flavour thresholds, interactions and recombination experiments. *Food Chemistry* **126**, 1679–1685.
- Torn, M.S. and Fried, J.S. (1992) Predicting the impact of global warming on wildland fire. *Climate Change* **21**, 257–274.
- Toth, L. and Wittkowski, R. (1985) Das räuchern – aus der sicht der chemie. *Chemie in unserer Zeit* **2**, 48–58.
- Ugrekheldidze, D., Korte, F. and Kvesitadze, G. (1997) Uptake and transformation of benzene and toluene by pkant leaves. *Ecotoxicology and Environmental Safety* **37**, 24–29.
- Ulrich, T. (2009) A perfect storm: how winemakers controlled wildfire smoke taint in 2008 juice, must and wine. *Wines & Vines* **January**, 64–67.
- Wasserman, A.E. (1966) Organoleptic evaluation of three phenols present in wood smoke. *Journal of Food Science* **31**, 1005–1010.
- Whiting, J. and Krstic, M.P. (2007) Understanding the sensitivity to timing and management options to mitigate the negative impacts of bush fire smoke on grape and wine quality – scoping study (Department of Primary Industries: Knoxfield, Vic., Australia). http://research.agwa.net.au/wp-content/uploads/2012/09/Smoke_Taint_Final_Report_2007.pdf [[accessed 11/6/15].
- Wilkinson, K.L. (2009) Amelioration of smoke derived taint in wine by membrane filtration and solid phase adsorption. Final report to Grape and Wine Research and Development Corporation, project number RD 06/04-2 (The University of Adelaide: Urrbrae, SA, Australia). http://research.agwa.net.au/completed_projects/amelioration-of-smoke-derived-taint-in-wine-by-membrane-filtration-and-solid-phase-adsorption/ [accessed 11/6/15].
- Wilkinson, K.L., Ristic, R., Pinchbeck, K.A., Fudge, A.L., Singh, D.P., Pitt, K.M., Downey, M.O., Baldock, G.A., Hayasaka, Y., Parker, M. and Herderich, M.J. (2011) Comparison of methods for the analysis of smoke-related phenols and their conjugates in grapes and wine. *Australian Journal of Grape and Wine Research* **17**, 522–528.
- Wilkinson, K.L., Pinchbeck, K.A., Ristic, R., Baldock, G.A. and Hayasaka, Y. (2012) Assessing smoke taint in grapes and wine. Qian, M.C. and Shelhammer, T.H., eds. *Flavour chemistry of wine and other alcoholic beverages*, Vol. 1104, ACS symposium series (American Chemical Society: Washington, DC, USA) pp. 57–65.
- Williams, A.A.J., Karoly, D.J. and Tapper, N. (2001) The sensitivity of Australian fire danger to climate change. *Climate Change* **49**, 171–191.
- Winters, A.J., Adams, M.A., Bleby, T.M., Rennenberge, H., Steigner, D., Steinbrecher, R. and Kreuzwieser, J. (2009) Emissions of isoprene, monoterpene and short-chained carbonyl compounds from Eucalyptus spp. in southern Australia. *Atmospheric Environment* **43**, 3035–3043.
- Wirth, J., Guo, W., Baumes, R. and Gunata, Z.J. (2001) Volatile compounds released by enzymatic hydrolysis of glycoconjugates of leaves and grape berries from *Vitis vinifera* Muscat of Alexandria and Shiraz cultivars. *Journal of Agricultural and Food Chemistry* **49**, 2917–2923.
- Wittkowski, R. and Baltus, W. (1990) Analysis of liquid smoke and smoked meat volatiles by headspace gas chromatography. *Food Chemistry* **37**, 135–144.

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