Alternative Perspective on Rapid Wine Oxidation through Changes in Gas-Phase Volatile Concentrations, Highlighted by Matrix Component Effects

Wenyao Zhu[1,2] [1] *Wine Science Programme, The University of Auckland, Private Bag 92019, Auckland, 1142, New Zealand;* [2] *Kim Crawford Winery, Constellation Brands NZ, 237 Hammerichs Road, Blenheim, 7273, New Zealand*; ORCID: orcid.org/0000-0001-7302-5178.

Frank Benkwitz[2] [2] *Kim Crawford Winery, Constellation Brands NZ, 237 Hammerichs Road, Blenheim, 7273, New Zealand*.

Paul A. Kilmartin[1*] Corresponding author – [1] *Wine Science Programme, The University of Auckland, Private Bag 92019, Auckland, 1142, New Zealand*; ORCID: orcid.org/0000-0003-2623-0958; Phone: +64 9 923 8324; Email: p.kilmartin@auckland.ac.nz.

Abstract

A new perspective is presented to investigate the sensorially relevant gas-phase concentrations of volatile compounds in wine. This is achieved by measuring the partition coefficients and matrix-phase concentrations of volatiles using static headspace-gas chromatography-ion mobility spectrometry (SHS-GC-IMS). Physicochemical properties that can contribute to the partition behaviors of ten volatile esters, such as hydrophobicity and matrix temperature, are also discussed. Partition coefficients are then linked to quantitative measurements to obtain partial pressures, which describes the availability of volatile compounds in the gas phase. The concept of partition coefficients and partial pressure have then been applied to a time series of aroma changes due to oxidation in commercial wines. As a follow-up study, a full factorial design was devised to inspect the impact of three common wine matrix components, namely, copper, polyphenols and ascorbic acid, on the partial pressure changes after 30-day oxidation treatment in either full-alcohol or low-alcohol simulated wine matrices. Interesting interactive effects between antioxidant behaviors and alcohol levels were elucidated, especially around the controversial use of ascorbic acid in winemaking. These results can guide winemakers who wish to minimize oxidative damage to wine aroma during wine storage or bulk transport, where ullage may be present or continual oxygen ingress may be occurring.

Keywords

static headspace-gas chromatography-ion mobility spectrometry (SHS-GC-IMS), wine, oxidation, partition coefficient, partial pressure, wine matrix components

1 Introduction

During any stage of winemaking, storage, and transport, oxidation has always been a major issue for winemakers and consumers alike. Multiple previous studies have shown that oxygen can alter the aroma profile of wines through an array of mechanisms, such as the quinone-related reactions[1-2] and the production of various carbonyl compounds using hydroxyl free radicals as intermediates (the Fenton Reaction)[2-4]. These changes tend to be harmful to the overall aroma of white wines, as important volatiles such as esters and varietal thiols that endow fruity attributes and varietal characters could be easily compromised.[5-6] However, the focus of ageing-related oxidative studies of wine aroma is on the changes that occur after prolonged storage for months or years, whereas the rapid oxidation events that occur in wine within several weeks of its exposure to an oxygen-rich atmosphere are not as widely studied.

An indirect perspective to approach this rarely researched phenomenon is the consumption rates of oxygen in O_2-enriched wine. For instance, Ferreira *et al*. reported that red wines enriched with oxygen from air (5.5–6.5 mg/L dissolved O_2) exhibited fast initial consumption rate of O_2 (averaged as 3.82 mg/L in the first day of oxidation).[7] A high initial consumption rate of O_2 was similarly observed by the same group in white and rosé wines, with copper, flavonols, and hydroxycinnamic acids shown to be the determining factors of the O_2 consumption rate.[8] Such findings were corroborated more recently by Kontoudakis and Clark, in that copper can drastically increase the rate of oxygen uptake in aerated wine within a short time frame.[9]

Additionally from the aroma perspective, Nikolantonaki and Waterhouse have reported that the first-order reaction constant k between 4-methyl-1,2-benzoquinone (a model quinone) and an important varietal thiol, 3-mercaptohexanol (3MH), is 0.0578 s^{-1}, corresponding to the half-life of 3MH in this reaction as 12.0 s (calculated as $\frac{\ln 2}{k}$).[10] Although in reality the rate of quinone-thiol reactions would be governed by other external factors such as the presence of antioxidants, varietal thiols react readily with oxidation-induced reactive species, which subsequently leads to aroma loss. Undesirable sulfur-containing volatiles such as 2-furanmethanthiol and hydrogen sulfide may similarly react with quinones and form odorless quinone-volatile adducts, although with slowers reaction rates.[10] Also, Ferreira *et al*. tentatively identified the increased levels of some volatile phenols as the end-products of polyphenol oxidation using SPE-GC-MS.[8] These studies illustrate how oxidation in wines occurs rapidly following contact with oxygen, which is accompanied by a series of sensory alterations involving aroma loss and formation.

However, it remains unclear whether other important wine aroma compounds, such as esters, are so readily affected by oxidation-related reactions in wines exposed to air for a short time. One publication that investigated ester changes in air-exposed wines on a multi-day scale reported that both ethyl and acetate esters experienced ~50–100% loss over two-day trial time. Attributing these changes solely to oxidation reactions in wines may be doubtful, as the trial was conducted in open bottles and could thus also involve evaporative loss.[11] The focus of other research has been mainly on the evolution of these compounds over a relatively long time span of months or years. For example, Patrianakou and Roussis reported that several esters in wines declined by up to 87% of its original content during 270-day storage when bottled with air in the headspace, compared to an 83% drop in the same wine bottled with nitrogen. However, a shorter storage time (20 days) indicated no apparent difference in esters in wines stored either with air or nitrogen in the bottle.[6] According to Makhotkina and Kilmartin, hydrolysis reactions can lead to the decline in ester content in wines, with small first-order reaction constants from 2.10–10.8×10^{-8} s^{-1}, (assuming storage at room temperature), which corresponds to a half-life of 2.48–12.73 months.[12] Therefore, hydrolysis contributes only insignificantly, if any at all, to the aroma loss of wines subject to oxidation for a few days. More rapid oxidation reactions that could influence the wine aroma profile, on the contrary, have yet to be confirmed.

This study addressed rapid oxidation phenomena in wine during a 30-day period. The influence of oxidation on wine esters are examined from a new perspective, based upon a consideration of ester partition coefficients and gas-phase concentration following air-exposure to wines. The first aim of the current study was to develop and optimize a method based on static headspace-gas chromatography-ion mobility spectrometry (SHS-GC-IMS) for determining the partition coefficients of multiple volatile compounds in wine. Secondly, the changes of volatile partition coefficients *per se*, as well as the gas-phase concentration, which is calculated from combining the volatile partition coefficients and quantification results through Henry's Law, were determined before and after oxidation. In the third part, a full-factorial experiment was conducted using a simulated wine matrix to investigate the impact of different wine matrix components on the volatile partition coefficient and gas-phase concentration changes during oxidation.

2 Materials and Methods

2.1 Chemicals and reagents

10 ester aroma standards were used, including methyl acetate, isobutyl acetate, isoamyl acetate, hexyl acetate, ethyl butyrate, ethyl hexanoate, ethyl octanoate, ethyl isobutyrate, ethyl isovalerate, and ethyl 2-methylbutyrate. All analytical standards (> 98% purity) were purchased from Sigma-Aldrich (Taufkirchen, BY, Germany) and were stored in a 5 °C cool room prior to use.

Reagents and chemicals used for the $ABTS^{\cdot+}$ assay included the ABTS salt (> 98%) supplied by Roche (Basel, Switzerland), potassium persulfate (ACS reagent, > 99%), phosphate buffer saline (PBS) tablets supplied by Sigma-Aldrich (Taufkirchen, BY, Germany), and sodium hydroxide pallets supplied by Thermo Fisher Scientific (Waltham, MA, USA).

Reagents and chemicals used in the matrix component effects trials included HPLC-grade ethanol (> 99.5%) supplied by Sigma-Aldrich (Taufkirchen, BY, Germany), three phenolic compounds (> 98%, HPLC grade): (+)-catechin hydrate, caffeic acid, and quercetin dihydrate supplied by Sigma-Aldrich (Taufkirchen, BY, Germany), copper sulfate pentahydrate (> 98.5%) supplied by Jost Chemical (St Louis, MO, USA), L-ascorbic acid (> 99%) supplied by Redox NZ (Christchurch, New Zealand), ferric chloride hexahydrate (> 99%) supplied by ECP Labchem (Auckland, New Zealand), potassium metabisulphite (> 99.5%) supplied by Esseco (Trecate, Piedmont, Italy), potassium bitartrate (> 99.5%) supplied by Check Stab Instruments (Florence, Tuscany, Italy), 37% (*w/w*) hydrochloric acid supplied by Thermo Fisher Scientific (Waltham, MA, USA).

2.2 Wine samples

Two New Zealand Sauvignon Blanc (both of vintage 2020) wines were used for the method development and optimization, and the 30-day oxidation trial.

2.3 Quantification of volatile compounds

The method for the quantification of volatile compounds has been validated in our previous publication.[13] Briefly, for each sample, an aliquot of five milliliters was pipetted into a 20 mL headspace vial using a micropipette. Also, 50 µL of an internal standard (3-octanol) was added into each sample as a quality control measure. The headspace of the vial was then purged with nitrogen to protect the sample from potential oxidation while awaiting analysis.

2.4 Determination of partition coefficients

The partition coefficients of volatile compounds were determined following the phase ratio variation (PRV) method developed by Ettre, Welter and Kolb in 1993.[14] This method states that, when a volatile compound has reached thermodynamic equilibrium between headspace and matrix, the reciprocal of its GC peak area is in linear relationship with the headspace:matrix phase volume ratio, which can be mathematically represented as:

$$\frac{1}{A} = \frac{1}{f_i \times C_0 \times k_{h/m}} + \frac{1}{f_i \times C_0} \times \beta \quad (1)$$

where A is the peak area, f_i is the response factor of the detector, C_0 is the original concentration of the volatile in the matrix, $k_{h/m}$ is the partition coefficient of the volatile between headspace and matrix, β is the headspace and matrix phase ratio in the sample vial ($V_h : V_m$).

Equation (1) can be further simplified to $\frac{1}{A} = a\beta + b$, where a is $\frac{1}{f_i \times C_0}$ and b is $\frac{1}{f_i \times C_0 \times k_{h/m}}$. Since A and β can be experimentally measured, the partition coefficient can be calculated once the linear relationship is determined between $\frac{1}{A}$ and β. Hence the partition coefficient ($k_{h/m}$) can be easily calculated as $\frac{a}{b}$ using PRV.

The method designed for the determination of volatile partition coefficients using SHS-GC-IMS was based on the quantification method, with incubation time, injection rate, and the signal linearity being re-evaluated. In order to determine the optimal incubation time, an aliquot of 3 mL wine was placed in a 20 mL headspace vial and capped tight. The vial was then incubated at 40°C while being agitated at 250 rpm for a preset period of time, ranging from 2 to 20 minutes, in 2-minute intervals. The syringe injection rate of the sample headspace onto the GC column was optimized at five levels: 2, 5, 10, 20, 30 mL/min (equivalent to 33.3, 83.3, 166.7, 333.3, and 500 µL/s). Furthermore, the linearity of instrument responses for varying sample volumes was evaluated with the following volumes: 100 µL, 200 µL, 300 µL, 500 µL, 1000 µL, 1500 µL, 2000 µL, 2500 µL, 3000 µL. The linearity was determined by calculating the correlation coefficient (Pearson's R^2) accompanied by visual inspection. Linear correlation was recognized if $R^2 > 0.95$.

In summary, the optimized PRV method was conducted as follows. Nine different volumes (100 µL, 200 µL, 300 µL, 500 µL, 1000 µL, 1500 µL, 2000 µL, 2500 µL, 3000 µL) of the sample were pipetted into 20 mL headspace vials (precise volume of 20.54 mL) and arranged in ascending order of sample volumes for analysis. The addition of internal standard and the headspace purging with nitrogen were not needed in the PRV method.

2.5 Henry's Law and the partial pressure of volatile compounds

The Henry's Law states that, the concentration (C) of a gas dissolved in a liquid is directly proportional to the partial pressure (p) of the gas above the liquid. Mathematically such a relationship can be expressed as $C = kp$, where k is the Henry's Law constant.[15] Dependent of the concentration – pressure relationship that needs to be modelled, the Henry's Law constant can take several forms, one of which is the dimension-less Henry's Law constant and is numerically equivalent to the partition coefficient described in section 2.4.[16] In systems where the solutes of interest are dilute with respect to the solvent, the activity coefficients of solutes do not depart considerably from 1, and hence the fugacity of volatile compounds obeys Henry's Law.[17] Indeed, other authors have applied the idea of Henry's Law in more abundant volatile components of wine, e.g., the sulfur dioxide.[18] Therefore, with both partition coefficients and concentrations determinable for all volatile compounds in this study, the partial pressure can then be calculated following the Henry's Law. Specifically, the partial pressure of volatile compounds (p_{volatile}) was calculated as follows[15]:

$$p_{\text{volatile}} = 10^6 \times \left(RT H_{\text{v}}^{cc} \cdot \frac{C_0 \times 10^{-6}}{M} \right) \quad (2)$$

where R is the ideal gas constant (8.3145 L kPa K^{-1} mol^{-1}), T is the analysis temperature in K (313.15 K in this study), H_{v}^{cc} is the dimension-less Henry's Law constant, C_0 is the concentration of the aroma compound in wine in µg/L, M is the molar mass of the volatile compound in g/mol, 10^6 and 10^{-6} are the factors to convert the unit of p_{volatile} to mPa (milli-Pascal).

Additionally, in consideration of possible partition coefficient changes before and after a certain treatment (e.g., oxidation), the quantification results, and hence the volatile partial pressure, of samples after the treatment were adjusted accordingly by multiplying with the adjustment factor calculated using equation (3). In this calculation, k_0 and k_1 represents the partition coefficients before and after the treatment, respectively, and β represents the headspace and matrix phase ratio. The adjustment factor was based on the theoretical background of static headspace sampling technique described by Kolb as shown in equation (4).[19]

$$\text{adjustment factor} = \frac{k_0 + \beta k_0 k_1}{k_1 + \beta k_0 k_1} \quad (3)$$

$$C_{\text{HS}} = \frac{C_0}{k_{m/h} + \beta} = \frac{k_{h/m} \cdot C_0}{1 + k_{h/m} \cdot \beta} \quad (4)$$

where C_{HS} is the analyte concentration in the container headspace at equilibrium, C_0 is the analyte concentration in the sample matrix before partitioning into headspace occurs, $k_{h/m}$ is the headspace-matrix partition coefficient, $k_{m/h}$ is the reciprocal of $k_{h/m}$, and β is the phase ratio.

2.6 Instrument conditions of SHS-GC-IMS

Instrumentation and method parameters were used as reported in our previous study.[20] The G.A.S. FlavourSpec SHS-GC-IMS instrument used in the current study was purchased from Gesellschaft für Analytische Sensorsysteme mbH, Dortmund, Germany. An MXT-WAX polar column (30 m length × 0.53 mm internal diameter × 0.5 µm film thickness, 100% crossbond Carbowax polyethylene glycol stationary phase) was purchased from RESTEK (Bellefonte, PA, USA). The instrument was also connected to an autosampler (CTC Analytics AG, Zwingen, Switzerland) for the automated sample handling.

Each sample vial was incubated at 40 °C for 10 minutes and 12 minutes for quantification and partition coefficient determination samples, respectively, before 500 µL of the headspace was extracted through a heated (80 °C) syringe and injected via a heated injection port onto the GC column. The GC column was programmed to operate isothermally at 40 °C, whereas the separation of compounds was facilitated using a flow rate ramp of the GC carrier gas. Specifically, the flow of carrier gas (nitrogen, > 99.95% purity) was initially set at 2 mL/min for one minute, and then gradually increased to 40 mL/min at a rate of 2 mL/min^2 until 20 min. Then the flow rate was instantly raised to 150 mL/min and held at this rate until 50 min. Then for additional two minutes, the flow rate was decreased back to 2 mL/min, before the program concluded.

An IMS device was attached immediately after the GC separation for a second separation dimension. The IMS ionization was realized using a tritium (^{3}H) source in positive mode. Ionized compounds then entered the IMS drift tube (98 mm, set at 75 °C) and travelled towards the Faraday Plate detector at the end of the drift tube under a constant electric field (500 V/cm). A drift gas (nitrogen, > 99.95% purity) of constant flow rate (150 mL/min) travelling in the opposite direction of the ion flow was able to differentially retard the movement of the

compound ions according to their sizes and shapes, which results in different arrival times at the detector and hence the differentiation of compounds. Each IMS spectrum was acquired as the average of six scans.

2.7 Miscellaneous methods for oxidation-related parameters in wine

2.7.1 Copper and iron

The elemental analyses of copper and iron was performed using Agilent 4200 microwave plasma-atomic emission spectroscopy (MP-AES) device (Agilent Technologies, Santa Clara, CA, USA), following an internally developed protocol at the Kim Crawford Winery. Briefly, a total volume of 10 mL per sample was decanted into a glass test tube for analysis. An external matrix-matched calibration was performed daily using a Sauvignon Blanc wine with known amount of elemental copper and iron spiked with commercially available 1 g/L copper dinitrate in 1 M nitric acid solution (Fisher Chemical, Auckland, New Zealand) for copper analyses, or spiked with commercially available 1 g/L ferric nitrate in 5% *m/m* nitric acid solution (Agilent Technologies, Santa Clara, CA, USA). Elemental copper and iron were detected at wavelengths of 324.8 nm and 259.9 nm, respectively.

2.7.2 Free sulfur dioxide and 420 nm absorbance (browning index)

The determination of free sulfur dioxide (FSO_2) and 420 nm absorbance (browning index) was conducted using the FOSS WineScan™ instrument (Hillerød, Denmark). Briefly, 25 mL of the sample was decanted into a 30 mL flat-bottom tube for analysis. Calibrations of FSO_2 and browning index were conducted regularly against established manual methods.[21] Additionally, daily checks were performed to ensure the accuracy of FSO_2 measurements using a commercial Sauvignon Blanc wine with known FSO_2 concentration.

2.7.3 Total antioxidant capacity

The total antioxidant capacity (TAC) method was adopted from Paixão *et al.*[22], and Baltrušaitytė, Venskutonis and Čeksterytė[23] with minor modifications. Briefly, the $ABTS^{\cdot+}$ radical was firstly prepared by adding 0.055 g of 2,2-azino-bis-(ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) into 50 mL phosphate buffered saline (PBS, prepared per manufacturer instructions from tablets) to produce the 2 mM $ABTS^{\cdot+}$ stock solution. The pH of the $ABTS^{\cdot+}$ working solution was then checked and adjusted to 7.4 if necessary, using 0.1 M sodium hydroxide (NaOH) solution. A 70 mM potassium persulfate ($K_2S_2O_8$) stock solution was also prepared by dissolving 0.189 g of potassium persulfate into 10 mL Type 1 water (resistivity > 18 MΩ/cm) supplied from a Sartorius arium® pro VF Ultrapure Water System (Göttingen, Germany). The final $ABTS^{\cdot+}$ working solution was then prepared by adding 100 µL of potassium persulfate stock solution into the 50 mL $ABTS^{\cdot+}$ stock solution.

The $ABTS^{\cdot+}$ working solution was allowed to react under room temperature in the dark for 16 hours. Subsequently, the $ABTS^{\cdot+}$ working solution was further diluted in 1:8 dilution using PBS to reach the absorbance of 0.80 ± 0.05 at 734 nm. The measurements were taken using a Genesys™ 10 UV Spectrophotometer from Thermo Fisher (Rochester, NY, USA).

At the start of each analysis sequence, pure PBS was first analyzed as a blank correction. For each wine sample, 12 µL of the wine was added into 3 mL of the $ABTS^{\cdot+}$ working solution and thoroughly mixed using a vortex mixer for 10 s. The absorbance (734 nm) of the sample was acquired under room temperature during 20 minutes in 5-minute intervals. The total antioxidant capacity was expressed as the $ABTS^{\cdot+}$ inhibition rate (I) and calculated as $I = \left(\frac{A_{\text{intial}} - A_{\text{sample}}}{A_{\text{intial}}}\right) \times 100\%$, where A_{sample} is the absorbance of the reacted wine sample and A_{intial} is the absorbance of the $ABTS^{\cdot+}$ working solution. All absorbance measurements were corrected according to the blank correction.

2.8 30-day wine oxidation trial

A 30-day wine oxidation trial was set up to investigate the potential changes to the partition coefficients and the partial pressure of volatile compounds due to oxidation over a 30-day period, which were monitored in 5-day intervals, *i.e.*, samples were taken at Day 0, 5, 10, 15, 20, 25, 30 from the start of experiment. The Day 0 sample was acquired directly from the freshly opened bottle of wine. For each of the remaining six sampling dates, 330 mL wine was decanted into a one-liter Schott bottle. All six bottles were then gently shaken for 90 s, after which the content was exposed to undisturbed static air for 180 s to ensure air saturation in the wine. The effect of the air saturation treatment was validated by subjecting 330 mL of the same commercial Sauvignon Blanc wine (identical bottling batch) to the cumulative duration of shaking and air-exposure straight after opening, and analyzing the wine before and after the treatment. Additionally, it has been previously reported that the loss of volatile compounds in wine due to evaporation tends to occur in a short timeframe (120 mins) after exposure to open air.[24] It was therefore confirmed that this treatment *per se* did not induce statistically significant differences in the concentrations of the studied volatile compounds ($p > 0.114$). Hence, it was concluded that the air saturation treatment did not result in evaporative loss of volatile compounds. After air exposure, the bottles were tightly capped and wrapped with aluminum foil and placed away from direct light at room temperature (21 °C). Such air saturation treatments were performed every other day, until the date when the bottle was ready for instrumental analysis.

2.9 Effects of matrix components on volatile compound changes during oxidation

A full factorial experimental design was conducted to investigate the effects of four common components in the wine matrix, namely, ethanol, polyphenols, copper, and ascorbic acid, on the changes in wine volatile compounds during a 30-day oxidation trial. A base simulated wine matrix was initially prepared, which contained 3.36 g/L potassium bitartrate (equivalent of 2.0 g/L bitartrate ion ($C_4H_5O_6^-$), calculated using the Henderson-Hasselbalch equation), 7.2 mg/L ferric chloride hexahydrate (equivalent of 1.5 mg/L ferric ion), and 43.5 mg/L potassium metabisulfite (equivalent of 25.1 mg/L free SO_2 using empirical conversion factor of 0.576). The pH of the simulated wine was subsequently adjusted to 3.2 using 6 M aqueous hydrochloric acid solution where necessary. The use of sulfur dioxide was necessitated by the involvement of ascorbic acid in the setups, which, when not used in conjunction with SO_2, can result in pro-oxidant activities rather than function as an antioxidant.[25] Also, the addition of potassium bitartrate and ferric chloride was justified by the critical involvement of tartrate ions and iron in oxidation reactions.[26-27]

Additionally, a subset of the four matrix components (ethanol, polyphenols, copper, and ascorbic acid) were added to the base simulated wine matrix to produce a unique configuration. The levels of polyphenols, copper and ascorbic acid were set such that they approximate the higher end of their actual ranges in commercial Sauvignon Blanc wines and are listed as follows:

1. Ethanol: 7% or 12%;
2. Polyphenols: either addition or blank. Added polyphenols contained 99.7 mg/L of caffeic acid, 10.4 mg/L of catechin, 10.2 mg/L of quercetin;
3. Copper: either addition or blank. Added copper ion amount into the simulated wine matrix was 0.51 mg/L;
4. Ascorbic acid: either addition or blank. Added ascorbic acid amount into the simulated wine matrix was 50.1 mg/L.

A total of 16 configurations were therefore prepared, whose run order was fully randomized and summarized in Table 1.

Table 1. Run order and the levels of matrix components used in all 16 simulated wine matrices for investigating the effects of 30-day oxidation on wine volatiles.

Run order	Ethanol	Polyphenols	Copper	Ascorbic acid
A	12%	addition	blank	addition
B	12%	blank	addition	blank
C	7%	addition	blank	addition
D	12%	blank	blank	blank
E	7%	addition	addition	addition
F	12%	blank	addition	addition
G	7%	blank	addition	blank
H	7%	blank	blank	blank
I	7%	blank	addition	addition
J	7%	addition	blank	blank
K	12%	addition	addition	blank
L	12%	blank	blank	addition
M	7%	blank	blank	addition
N	12%	addition	blank	blank
O	7%	addition	addition	blank
P	12%	addition	addition	addition

Each of the 16 configured wine matrices was then spiked with an aroma mix that contained 10 volatile compounds found in wines. Details of these 10 compounds and their spiked concentrations can be found in Supporting Table S1.

Following the same oxidation procedure outlined in the 30-day wine oxidation trial section, the partition coefficients and the partial pressure of volatile compounds were measured as "fresh" and "oxidized". Similarly, additional parameters, including FSO_2 and the total antioxidant capacity, were also determined before and after the oxidation treatment.

2.10 Statistical analyses

Peak signal intensities of SHS-GC-IMS measurements were acquired using the quantitation module of the Laboratory Analytical Viewer (LAV version 2.2.1, Dortmund, Germany) as volume-under-the-shape. Raw data were collated, and basic calculations were performed using Microsoft Excel 2019 (Redmond, WA, USA). Advanced data processing tasks, such as ANOVA analyses, plot creation, factorial design analyses, was conducted using the programming language R (version 4.0.2, Vienna, Austria). The significance level was set at 5% for all *post-hoc* Tukey's HSD tests of ANOVA. The error bars of all plots where they are available indicate the range of ± standard error.

3 Results and Discussion

3.1 Method development for determining volatile partition coefficients

Since the method for determining the volatile partition coefficients aimed to cover a wide range of sample volumes (100–3000 µL), it was decided that the highest sample volume (3 mL) would be selected for the optimization of sample incubation time and injection rate. Since the current study concerns the rapid oxidation of volatile compounds, the passive equilibration reported in previous publications,[28] *i.e.*, awaiting volatile compounds to naturally disperse from the liquid into the headspace, was thus deemed inappropriate as prolonged equilibration time would potentially introduce additional oxidation to the sample. Moreover, the

incubation temperature of 40 °C was selected as it mimics the orthonasal and retronasal perception of humans,[29] along with agitation at 250 rpm.

A range of incubation times from 2 min to 20 min was tested to identify the minimum time needed for volatile compounds to reach equilibrium in the headspace. As shown in Supporting Figure S1, the signals of all ten esters in the 3 mL sample reached a maximum after 12 minutes of incubation, with no additional statistically significant (p = 0.05) variations with a further increase in the incubation time, which indicates that the headspace/matrix equilibria were attained for these compounds.

As mentioned by Athès et al., lower injection rate (100 µL/s) can significantly increase the chromatographic signal compared to higher rates (250–600 µL/s).[30] This effect was also observed in the current study, but it only applied to three of the ten esters, namely methyl acetate, ethyl butyrate and isoamyl acetate (Supporting Figure S2 (A)). All other compounds did not demonstrate discernible differences in signal intensities at different injection rates. This limited benefit of lower injection rates was also observed by Cameleyre, Lytra and Barbe.[28] However, a lower injection rate led to some distortion of peak shapes, especially for methyl acetate and ethyl isobutyrate, which showed tailing on either GC or IMS dimensions (Supporting Figure S2 (B and C)). In light of such detrimental effects, the medium injection rate of 10 mL/min (166.7 µL/s) was selected for this study, to maintain the desirable morphology of the peaks.

Since the calculation of partition coefficients is based on the underlying assumption that a linear relationship exists between the reciprocal of signal intensity and the phase ratio,[14] such a linearity was validated for all volatile compounds across the sample volume range of 100 to 3000 µL. It can be seen from Table 2 that the minimum value of the coefficient of determination (R^2) was 0.9702 for isoamyl acetate. The R^2 values for all other compounds were higher than 0.98, which demonstrates satisfactory linearity[31] and thus ensures the integrity of the PRV method. Moreover, previous research has reported considerably more narrow linear ranges for the concentration-signal relationship with IMS detectors.[13] It is advisable that the R^2 values be examined each time for a new volatile compound and/or sample matrix, and dilution be applied should the linearity fail.

Table 2. The signal linearity values of partition coefficient method validation using SHS-GC-IMS.

Compound	Injected volumes	Linearity of Signals (R^2)	Compound	Injected volumes	Linearity of Signals (R^2)
Methyl acetate	100–3000 µL	0.9847	Isobutyl acetate	100–3000 µL	0.9976
Isoamyl acetate	100–3000 µL	0.9702	Hexyl acetate	100–3000 µL	0.9983
Ethyl butyrate	100–3000 µL	0.9860	Ethyl hexanoate	100–3000 µL	0.9923
Ethyl octanoate	100–3000 µL	0.9980	Ethyl isobutyrate	100–3000 µL	0.9981
Ethyl isovalerate	100–3000 µL	0.9969	Ethyl 2-methylbutyrate	100–3000 µL	0.9976

3.2 Partition coefficients of volatile esters in wine

A vintage 2020 Sauvignon Blanc wine was tested to investigate the partition behavior of ten esters commonly found in this wine variety. These esters include four acetate esters (methyl acetate, isobutyl acetate, isoamyl acetate, hexyl acetate), three straight chain ethyl esters (ethyl butyrate, ethyl hexanoate, ethyl octanoate), and three branched-chain ethyl esters (ethyl isobutyrate, ethyl isovalerate, ethyl 2-methylbutyrate). It can be seen from Figure 1 (series 12% alcohol) that the partition coefficients of these compounds vary vastly by up to a factor of 20 (methyl acetate *vs* ethyl octanoate), which indicates how different the releasability can be for these volatiles into the headspace from wine.

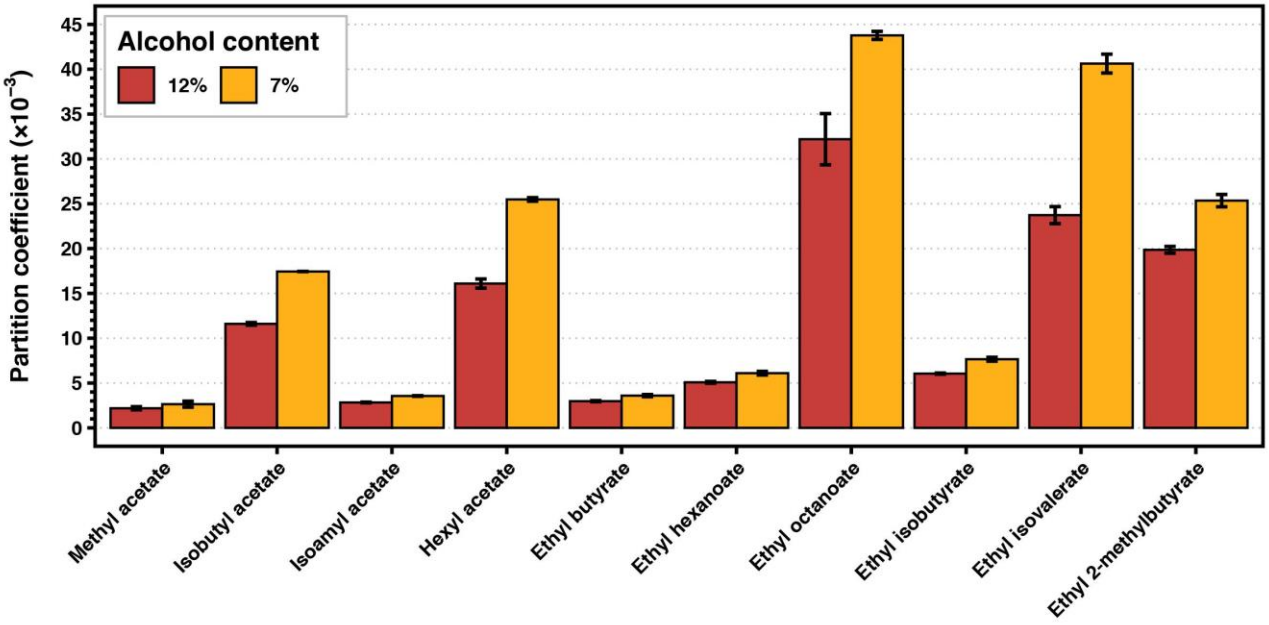

Figure 1. The partition coefficients of 10 volatile esters determined in full-alcohol (12%) and low-alcohol (7%) commercial Sauvignon Blanc wines.

Considering the respective octanol-water partition coefficients (log *p*), which are commonly used to define compound polarity (see Supporting Table S2), the partition of these esters in wine correlates positively with the degree of hydrophobicity. This effect has been observed by other researchers. For example, a spike was observed in partition coefficients for ethyl esters with longer aliphatic chains (C_3–C_8) in pure dilute hydroalcoholic solution (12% *v/v*) and when supplemented with tannins, as reported by Cameleyre *et al.*[32] Similarly in a different food matrix, Martuscelli *et al.* demonstrated that, compared to the aroma partition in custard made from full fat milk (3% milk fat), in custard made from skim milk, ethyl butyrate, ethyl isovalerate and ethyl hexanoate had seen 2.5-fold, 4.8-fold and 10-fold increases in partition coefficients, respectively.[31]

Being the most abundant non-aqueous component in wine, ethanol has been shown to increase the solubility of volatile esters and thus decrease their headspace availability.[33-34] This can be explained by the lower relative polarity of ethanol (0.654, with water set as 1),[35] and hence the lower overall polarity of wine. To further explore the influence of alcohol content on the partition behavior of volatile esters, another trial was set up using a low-alcohol wine (7% alcohol). Statistically significant ($p = 0.05$) differences were observed for all volatile esters except methyl acetate (Figure 1, series 7% alcohol), which, as discussed previously, is the most hydrophilic member of the group. The important role of hydrophobicity is further corroborated by the trend that the more hydrophobic esters, including hexyl acetate, ethyl octanoate and ethyl isovalerate, coincide with the highest levels of increase in partition coefficients (35.9–71.2% increase) when alcohol content was decreased from 12% to 7%. Interestingly, the similarly hydrophobic ethyl 2-methylbutyrate was less affected, which indicates that additional factors other than hydrophobicity may contribute to the partitioning of volatile compounds. The impact of varying alcohol levels has been previously described by multiple authors, either through direct inspection on volatile partitioning[36-37] or as an indirect observation during the development of static headspace-based quantification methods.[13]

Moreover, although alcohol is present in wine in relatively large amounts, Conner *et al.* stated that only ethanolic solutions of concentrations higher than 17% (*v/v*) could alter the activity coefficient of esters,[38] due to the formation of hydrophobic ethanol micelles[39] and the enhanced hydrophobic interactions between ethanol micelles and esters. Therefore, given the common alcohol concentrations of wine (around 7–15%), the system

can essentially be regarded as aqueous, which renders hydrophobicity a predominant driving force that governs ester partition from the wine matrix.

When considering both the human physiological sensitivity towards different types of volatile compounds (*e.g.*, ethyl esters or acetate esters), and that the partition coefficients describe the phase preference of volatiles, a link may thus be postulated between the odor thresholds of volatile compounds and their respective partition coefficients. A collation of odor thresholds of the ten esters investigated in this study is presented in Supporting Table S3. It can be seen that the odor threshold values of acetate esters are only available from a diverse range of matrices, while the matrices used for ethyl ester odor thresholds are much more unified. As a result, partition coefficients and odor thresholds indeed form a linear correlation on a log-log scale with a power function curve for all six ethyl esters examined (R^2 = 0.9282, see Supporting Figure S3). The similar log-log relationship has also been previously reported by Abraham *et al.*, who also indicated that the octanol-water partition coefficients are important in transporting the volatile molecules through the nasal mucosa.[40] Therefore, it can be evidenced that, in conjunction with the previous discussion, the ladder of hydrophobicity followed by ethyl esters functions as the major determinant for the release and perception of these compounds.

The partition coefficient values obtained in the current work were also compared to those obtained from other studies. Given the fact that the partition coefficient is strongly dependent of temperature under which the measurement was taken, values are thus not directly comparable. The temperature dependence of partition coefficients can be mathematically modelled using the van 't Hoff equation[41]:

$$k_{h/m}(T) = k_{h/m}^{\ominus} \times \exp\left[-\frac{\Delta_{\mathrm{sol}}H}{R} \times \left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right] \quad (5)$$

where $T^{\ominus}$ and $k_{h/m}^{\ominus}$ are the reference temperature (25 °C, 298.13 K) and the partition coefficient at the reference temperature, T and $k_{h/m}(T)$ are the target temperature and the partition coefficient under this target temperature, $\Delta_{\mathrm{sol}}H$ is the enthalpy of dissolution, and R is the ideal gas constant. The values of $k_{h/m}^{\ominus}$ and $\frac{\Delta_{\mathrm{sol}}H}{R}$ for all ten esters are tabulated in Supporting Table S4. The values of $\frac{\Delta_{\mathrm{sol}}H}{R}$ diverge considerably from those obtained in binary water-volatile mixes,[15] indicating the greatly modified temperature dependence of volatile partitioning in complicated matrices such as wine. Also, it was noted that discrepancies invariably exist, of varying degrees, between the van 't Hoff-extrapolated partition coefficient values of the current study and those presented in other publications. This could, at least partially, be attributed to the heterogeneity amongst the matrices used in different studies and hence the presence/absence of specific components. Matrix components, either volatile or non-volatile, have previously been reported to impact the partition coefficients of volatile compounds.[28, 42] Nevertheless, the current results can constructively facilitate comparisons with partition coefficients obtained in future research.

3.3 Oxidation-induced changes in wine: focusing on esters in headspace

3.3.1 Oxidation-related parameters

Three bottles of vintage 2020 Sauvignon Blanc wines from the same production batch were mixed before being distributed into six one-liter Schott bottles for the oxidation trial. General parameters related to oxidation and polyphenols were monitored during the 30-day period and recorded in 5-day intervals. As shown in Supporting Table S5, the free SO_2 demonstrated a consistent decrease throughout the 30-day period, which indicates the continual occurrence of oxidation in the wine.[43] Moreover, the absorbance at 420 nm, which is often used as an indicator of browning in white wines, increased by 30% from 0.073 to 0.095, which demonstrates the formation of polyphenol condensation products.[44] Also, the effects of oxidation are seen from the 11% decrease of the total

antioxidant capacity (TAC) measured with the ABTS method. As catalysts of the oxidation process, iron and copper were both detected in the wine and, in alignment with expectations, their concentrations did not change throughout the oxidation process.

3.3.2 Partition coefficients

The partition coefficients for the ten volatile esters, on the other hand, did not vary greatly during the oxidation period, as summarized in Table 3. Ethyl octanoate demonstrated the most consistent gradual decrease in partition coefficient to 78% of its original value. The branched chain ethyl esters, ethyl isobutyrate, ethyl isovalerate and ethyl 2-methylbutyrarte, also showed a significant decrease in partition coefficients but in a more heterogeneous fashion. The partition coefficients of these three compounds in fact increased for the first 25 days of oxidation and then declined sharply during the 25–30 day period. Other compounds with lower hydrophobicity, did not show statistically significant changes in partition coefficients, indicating minor differences in their releasability from oxidized wine into the headspace compared to fresh wine.

Table 3. Headspace-matrix partition coefficients of ten volatile esters in Sauvignon Blanc wine and their evolution over a 30-day oxidation period. For each compound (row-wise), values bearing different letter notations indicate statistically significant difference.

Compound	Headspace-matrix partition coefficient ($k_{h/m}$, $\times 10^{-3}$, 40 °C)						
	Day 0	Day 5	Day 10	Day 15	Day 20	Day 25	Day 30
Methyl acetate	2.19 (0.08) *a*	1.43 (0.07) *b*	1.51 (0.11) *b*	1.97 (0.09) *ab*	1.9 (0.1) *ab*	1.82 (0.07) *ab*	2.09 (0.1) *a*
Isobutyl acetate	11.6 (0.07) *bc*	12.13 (0.13) *ac*	12.1 (0.34) *ac*	11.93 (0.18) *ac*	13.29 (0.34) *ab*	13.57 (0.32) *a*	10.91 (0.4) *c*
Isoamyl acetate	2.83 (0.02) *ab*	2.65 (0.08) *ab*	2.53 (0.13) *b*	2.8 (0.02) *ab*	2.96 (0.09) *a*	2.79 (0.03) *ab*	2.72 (0.05) *ab*
Hexyl acetate	16.1 (0.24) *b*	17.1 (0.18) *ab*	16.99 (0.47) *ab*	17.17 (0.21) *ab*	19.05 (0.48) *a*	16.96 (0.45) *a*	18.7 (0.52) *a*
Ethyl butyrate	2.98 (0.03) *ab*	2.94 (0.05) *ab*	2.86 (0.1) *ab*	2.99 (0.02) *ab*	3.19 (0.07) *a*	2.69 (0.06) *a*	3.17 (0.02) *b*
Ethyl hexanoate	5.08 (0.05) *c*	5.03 (0.1) *c*	5.04 (0.18) *c*	5.2 (0.03) *bc*	5.81 (0.15) *ab*	5.07 (0.1) *a*	6.25 (0.09) *c*
Ethyl octanoate	32.2 (1.32) *a*	29.16 (0.7) *ab*	27.9 (0.9) *ab*	24.1 (0.8) *b*	26.85 (0.93) *b*	25.18 (0.47) *b*	24.06 (0.45) *b*
Ethyl isobutyrate	6.05 (0.03) *c*	6.21 (0.06) *bc*	6.25 (0.15) *bc*	6.31 (0.05) *bc*	6.81 (0.15) *ab*	5.73 (0.15) *a*	7.24 (0.12) *c*
Ethyl isovalerate	23.73 (0.44) *c*	25.61 (0.44) *ac*	25.58 (0.94) *ac*	24.45 (0.53) *bc*	29.23 (1.19) *ab*	16.64 (1.15) *a*	30.36 (0.45) *d*
Ethyl 2-methylbutyrate	19.86 (0.17) *b*	20.58 (0.31) *b*	21.31 (0.81) *ab*	20.49 (0.25) *b*	22.76 (0.76) *ab*	12.08 (0.69) *a*	24.54 (0.36) *c*

The decline in the partition coefficients of some of the esters may be related to the binding of phenolic compounds as a result of oxidation, and the subsequent hydrophobic interactions between the resultant oligomeric phenols and esters. The exact structures of these polymerization products, however, remain poorly known, and have only been tentatively proposed based on the mass fragmentation using tandem mass spectrometry.[45] Indirectly still, the investigation of a-, b- and c-type of procyanidins (condensed tannins), which are dimers and trimers of flavonoids, reveals that their theoretical hydrophobicity (log *p* values) are much greater than the constituent monomeric catechin and epicatechin (> 3.7 for trimers, > 2.3 for dimers, 1.37 for

monomer, estimated from www.molinspiration.com). Hence, it could be hypothesized that oxidation-induced polyphenol polymerization products, albeit with unclear structures, similarly possess higher hydrophobicity.

Indeed, Mitropoulou and coworkers have reported that the more hydrophobic ethyl octanoate is more likely retained inside the matrix due to tannins, whereas the comparatively hydrophilic counterparts, *e.g.*, ethyl hexanoate and isoamyl acetate, remain less affected.[46] Also, Lorraine *et al.* found that the branched structure of some esters could lessen the extent of ester-polyphenol hydrophobic interactions due to steric hinderance.[47] Given that the formation of phenolic oligomers is a gradual process with increasing oligomer size throughout oxidation, this may explain the rise-and-drop trends in the partition coefficients observed for the three branched chain ethyl esters, indicating the hydrophobic interactions overwhelm the steric hinderance force beyond a certain critical point. Also, another mechanism that could modify phenolic compounds, and hence likely the extent of ester-polyphenol interactions, is the irreversible formation of sulfonic adducts between sulfur dioxide and polyphenols, which has been observed with model catechols and two phenolics commonly found in Sauvignon Blanc wines, namely, (+)-catechin and caffeic acid.[48-49] However, more research, such as NMR-based analysis, is needed to closely inspect this phenomenon from a molecular level.

3.3.3 Partial pressure

From a physicochemical perspective, the Henry's Law offers invaluable insights to investigate the concentrations of aroma compounds that move from the matrix into the gas phase, *i.e.*, the headspace. Henry's law relates the partition coefficient to the matrix phase concentration of the volatile. Given that the headspace fraction of wine is directly perceived by human noses, the partial pressure of volatile compounds becomes more relevant for the sensory experience, contrasted with the mere quantification of volatiles.

Despite the generally recognized use of odor activity values (OAV) as an intuitive way of demonstrating the importance of a given volatile compound in food, a handful of concerns have been raised, including the high level of subjectivity and the consideration of a merely binary aroma-matrix system when obtaining odor threshold values.[50] The partition coefficient, on the other hand, overcomes these problems since it is objectively measured through an instrument method and accounts for potential thermodynamic impacts caused by other volatile and non-volatile components in the original matrix, which need to be excluded when determining odor threshold values using sensory panels. With the previously delineated relationship between odor thresholds and partition coefficients, the partial pressure, through combining the concentration and partition coefficient, can be used alongside the OAV to provide a more comprehensive depiction of the sensory impact of volatile compounds.

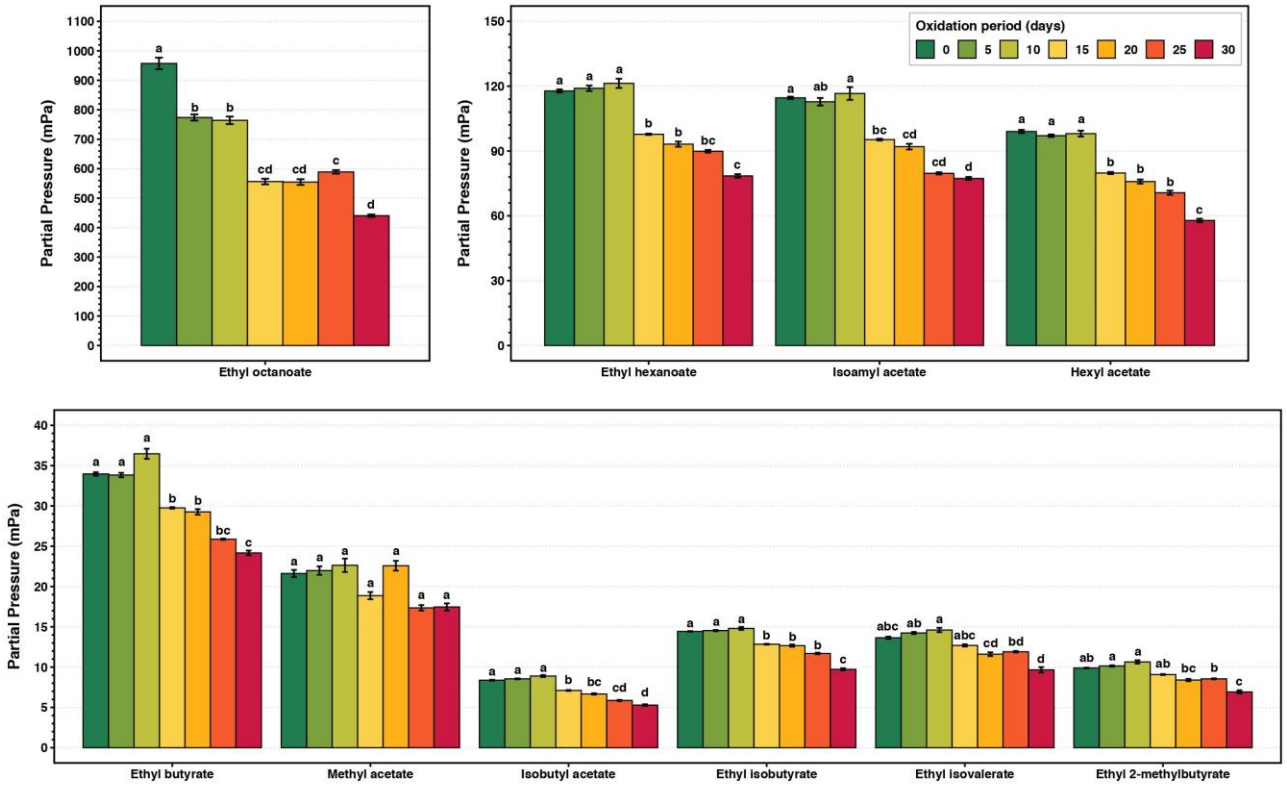

Figure 2. Changes in the partial pressure of ten volatile esters in wine during a 30-day oxidation trial. Bars of the same sample but with the different letter notations for each compound indicate statistically significant differences in signal intensities (Tukey's HSD, α = 0.05).

As can be seen in Figure 2 (series Day 0), ethyl octanoate possesses the highest partial pressure in the fresh wine, due to both its high concentration and high partition coefficient, followed by other major esters, including ethyl hexanoate, isoamyl acetate and hexyl acetate. In previous studies, ethyl octanoate, isoamyl acetate, and, to a lesser extent, ethyl hexanoate have been positively linked to the quality of Sauvignon Blanc wines, while a potential link was established between hexyl acetate and a lower Sauvignon Blanc quality grading.[20, 51] This effect could be explained by the gas-phase aroma concentrations of these compounds.

Different from the partition coefficients, the declining trend in partial pressure, as shown in Figure 2, was evident amongst almost all of the esters during the 30-day contact with air, with a decrease of between 19% and 54%. Overall, the partial pressure of ethyl octanoate after 30-day oxidation showed the greatest decline to 46% of its initial value. The partial pressure of ethyl hexanoate, hexyl acetate and isoamyl acetate also declined to 67%, 58% and 67% of their original values. From a sensory perspective, descriptors commonly associated with these compounds include "banana", "apple peel", "fruit" and "sweet" and "flower".[51] The decline of their respective partial pressure matches findings of a loss of fruitiness[52] and evidence for oxidation-related reactions in esters[53] exhibited for wine exposed to oxidative conditions. Therefore, changes in the partial pressure of volatile esters is complementary to existing research regarding the formation of acetaldehyde and other long-chain aldehydes and alcohols,[54] for their impacts on the perceived aroma of white wines during oxidation.

It should, however, be noted that the rate of decrease was not consistent. Specifically, only ethyl octanoate showed a significant decrease in partial pressure during Day 0 to 10, whereas values for the other compounds remained unchanged. Thus, any loss of fruitiness during the initial period of oxidation could be, at least partially, attributed to the change of ethyl octanoate within the headspace. From Day 10 onwards, the partial pressure of other compounds also started to gradually decline, which may induce further deterioration in the fruity

character of wine. Further studies, such as sensory evaluations conducted over finer time intervals, may assist with detailed tracking of aroma changes during oxidation.

3.4 Effects of matrix components on volatile esters during oxidation

Since wine is a highly complicated system in which many different compounds, each possessing its own physicochemicalproperties, are present, multiple matrix components have been shown to promote or retard wine oxidation, including copper(II), sulfur dioxide and ascorbic acid.[26, 43, 55] In order to describe the matrix component effects on the gas-phase concentrations of esters after oxidation, the partial pressure difference (PPD, denoted as Δp) was monitored for all compounds, and was calculated as follows:

$$\Delta p\ (\mathrm{PPD}) = \frac{p_{\mathrm{fresh}} - p_{\mathrm{oxidized}}}{p_{\mathrm{fresh}}} \times 100\% \quad (6)$$

where p_{fresh} and p_{oxidized} are the partial pressures of an ester in the freshly prepared and the oxidized matrices, respectively. Since the minimal loss of esters in gas-phase concentration, *i.e.*, the maximum retention of the original aroma, is desired, smaller Δp values are regarded as better and showing that a lesser aroma loss due to oxidation occurred. Negative values of Δp indicate an increase of volatile compound partial pressure after the oxidation period.

In this study, the effects of ethanol were not directly evaluated. Rather, the two different ethanol levels (7% *vs* 12%) were individually inspected to simulate how the gas-phase concentration of esters would react to oxidation in full alcohol wines and low alcohol wines. For each matrix component (copper, polyphenols, ascorbic acid), the change in PPD caused by its addition, was named C/PPD and calculated using equation (7), and possesses the same unit as that of PPD. The effects of all three components on the PPD were analyzed using three-way ANOVA, with fully decomposed simple effects analyses, where statistically significant interactions between multiple components were observed. The free sulfur dioxide and total antioxidant capacity values were also monitored as associated factors, and the results are summarized in Supporting Table S6.

$$\mathrm{C/PPD} = \mathrm{PPD}_{\mathrm{without\ component}} - \mathrm{PPD}_{\mathrm{with\ component}} \quad (7)$$

In the matrix component studies, the reciprocals of methyl acetate peak area and corresponding volume ratios failed to conform to linear relationships ($R^2 < 0.95$), which is a fundamental assumption in the PRV method. Therefore, the partition coefficients and partial pressure of methyl acetate were unable to be calculated and hence are not included in the discussions.

3.4.1 Visualization with cube plots

Given the large number of data points involved in the simple effects analyses, it was found that visualization of the results using the cube plot can most effectively convey the information. An explanatory sample of the cube plot structure is given in Figure 3. The edges colored in red, green and blue indicate the effects of copper, polyphenols and ascorbic acid, respectively. The pointing direction of arrows on these edges indicates the addition of a certain component into the matrix. The bottom left node represents the setup where all three components are absent, and the top right node represents the case where all three are present. The PPD values are then displayed next to the respective configurations (nodes, eight in total), while the C/PPD values are shown next to the respective component additions (edges, twelve in total) (see Supporting Figure S4).

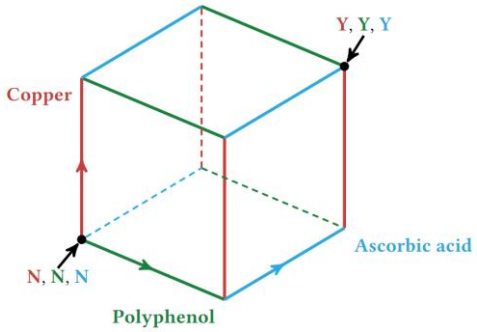

Figure 3. The structure of the cube plot representation of matrix component effects on the partial pressure changes during 30-day oxidation.

Although the cube plot can convey all information in the full factorial design, it lacks conciseness and is thus used only as a reference. All cube plots are provided in Supporting Figure S4. The information from the cube plots was further distilled and represented as bar plots and heatmaps, as discussed in the following sections.

3.4.2 Effects of matrix component combinations on partial pressure difference (PPD)

Amongst the three matrix components investigated, eight configurations can be generated. The denotations C, P and A are used to represent copper, polyphenols, and ascorbic acid, respectively. The number following the letter denotations, *i.e.*, 0 or 1, represents the absence or presence, respectively, of the corresponding matrix component. It can be observed from Figure 4 (A) and (B) that for full alcohol (12%) matrices, the combination of [C0, P1, A0] produced the lowest PPD value, *i.e.*, partial pressures of the nine esters showed minimal changes during the 30-day oxidation. Interestingly, in the grouped comparisons, acetate esters showed higher PPD values than the other two compound classes. The PPD values of the [C1, P1, A0] combination only showed statistically significant differences with those of [C0, P1, A0] for ethyl octanoate and the three branched chain ethyl esters, albeit with comparatively small changes (−2.6% for ethyl octanoate, averaged +6.9% for branched chain ethyl esters).

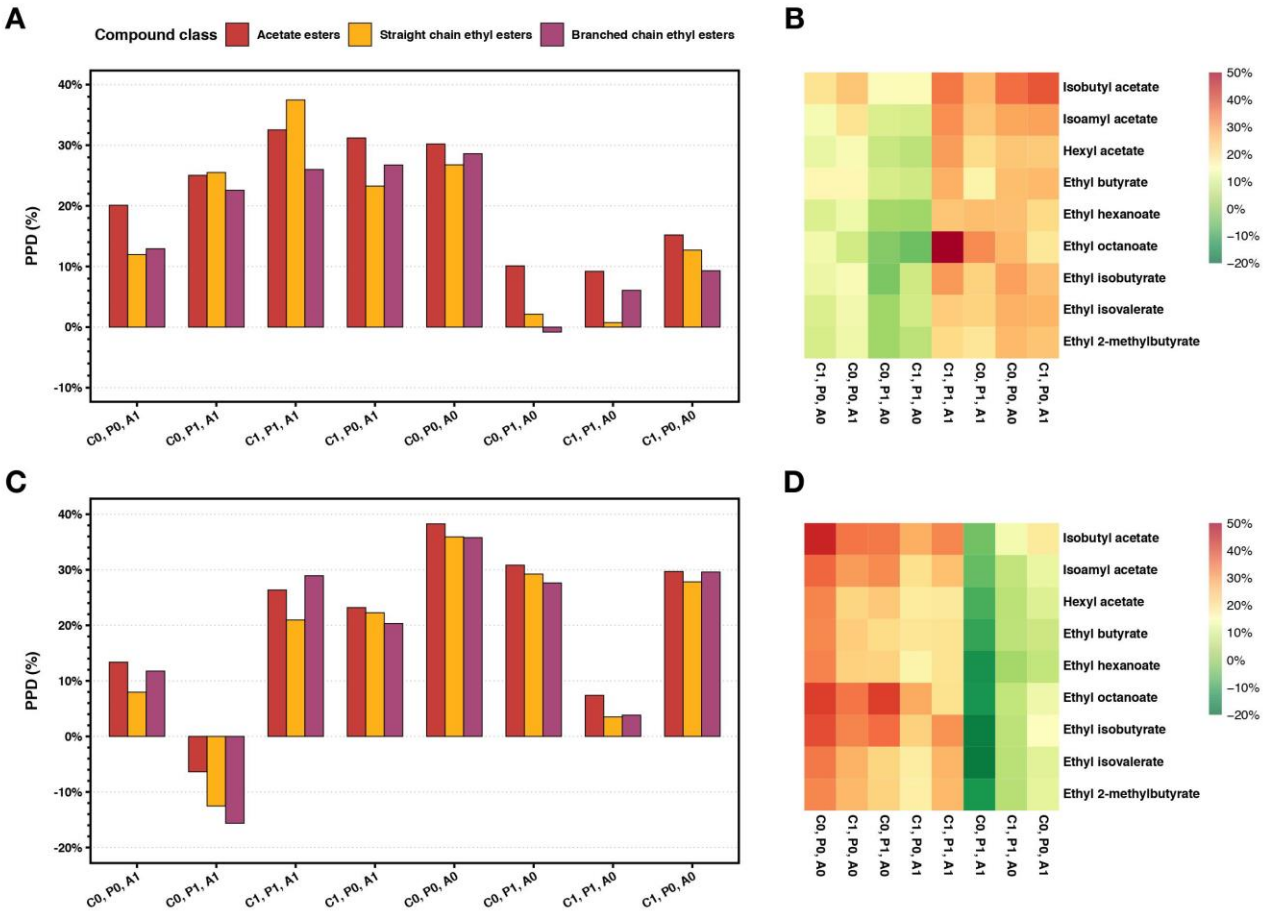

Figure 4. Effects of matrix component combinations on the partial pressure difference (PPD) during 30-day oxidation in simulated wine matrices. The denotations of component effects are formatted as follows: X0/1, Y0/1, Z0/1, where X, Y and Z indicates the different component (C for copper, P for polyphenols, A for ascorbic acid), and 0/1 indicates the absence/presence of the component. For example, C1, P1, A0 denotes the simulated matrix where copper and polyphenols are present and ascorbic acid is absent. (A) and (B): effects of component combinations on different volatile compound classes and on individual volatile compounds in full-alcohol (12% v/v) matrices. (C) and (D): effects of component combinations on different volatile compound classes and on individual volatile compounds in low-alcohol (7% v/v) matrices. Note that the order of matrix component combinations in heatmaps is sorted according to PPD effects similarity and are different from that shown in bar plots.

This finding highlights the importance of polyphenols in protecting volatile esters during oxidation. Similarly, Roussis and colleagues commented that, amongst 14 ethyl esters and 5 acetate esters, supplementation of caffeic acid at 100 mg/L to Muscat wine lowered the rate at which all 19 esters disappeared during oxidative storage. For instance, the loss of ethyl hexanoate, ethyl octanoate and isoamyl acetate was inhibited by 17.6%, 10.4% and 37.4%, respectively, in the presence of caffeic acid compared to control.[11] The use of copper is the go-to method should winemakers wish to suppress reductive off-odors such as hydrogen sulfide, although it also bears the negative impact of catalyzing oxidation reactions in wine.[56] However, in this trial, the application of copper did not induce considerable changes in the gas-phase concentration of esters after oxidation, provided that polyphenols are also present in the matrix. This could be attributed to the antioxidant role of polyphenols, which involves the Fe(II)/Fe(III) interchange catalyzed by copper.[43]

It must be noted, however, that the concentrations of polyphenols used in the current study are at their upper ends of concentrations found in Sauvignon Blanc wine.[57] Further, the addition of these polyphenols *per se* can decrease the partition coefficients of some volatile esters (*e.g.*, 16.2% decrease for that of ethyl octanoate), which lowers the fruitiness due to esters even prior to oxidation (see also section 3.2). Therefore, the positive impacts

of polyphenols on partial pressure changes after oxidation needs to be further examined using lower polyphenol concentrations.

The use of ascorbic acid in the full alcohol matrices mostly increased the PPD values, regardless of the compound class, compared to the configurations where ascorbic acid was not used. It can be seen from Figure 4 (A) that configurations with ascorbic acid induces high levels of volatile loss, given by PPD values up to 32.5%, 37.5% and 26.7% for acetate esters, straight chain ethyl esters and branched chain ethyl esters, respectively. Noticeably, when all three components were in the matrix ([C1, P1, A1]), ethyl octanoate suffered from the highest partial pressure decrease, *i.e.*, 58.6%, indicating severe compromise in the fruitiness perception (see Figure 4 (B)).

The auxiliary parameter FSO_2 indicated a clear difference between the averaged decline in free sulfur dioxide between all configurations with ascorbic acid (65.3%) and those without (60.7%), which points to a faster depletion of FSO_2 in the presence of ascorbic acid. Such pro-antioxidant phenomenon, which is due to the enhanced oxygen uptake by ascorbic acid, especially when the container headspace is O_2-enriched, has been previously reported and renders the wine inadequately protected from oxidation.[55] Ascorbic acid in full alcohol matrices clearly manifests pro-oxidant activity and loss of esters during oxidation, which defeats its intended use as an antioxidant.

On the other hand, the use of ascorbic acid in the low-alcohol matrices appeared more beneficial in retaining the gas-phase concentrations of volatile esters, as indicated by low PPD values (see Figure 4 (C) and (D)), especially when copper was not included in the matrix. Specifically, for all low-alcohol configurations with ascorbic acid, the PPD values of individual compounds were no higher than 33.2% in the presence of copper and 19.5% in the absence of copper, whereas it reached up to 58.6% for full-alcohol configurations with ascorbic acid. Free sulfur dioxide analyses also revealed that for all matrices containing ascorbic acid, those with 12% *v/v* alcohol averaged a 65.3% decline throughout the 30-day period, while the average decline of FSO_2 in 7% *v/v* alcohol matrices was lower at 62.6%, indicating better protection from oxidation in the lower-alcohol environment. Interestingly, the combined use of polyphenols and ascorbic acid in the absence of copper ([C0, PA, A1]), led to an increase in the partial pressure of the nine esters post-oxidation by 6.4–15.6%, which points to a synergistic effect of both antioxidants. A closer inspection at this configuration indicated the increase in partial pressure was mainly due to the rise in partition coefficients of all esters, while their original matrix-phase concentrations did not change as severely pre- and post-oxidation. For example, the averaged relative increase in partition coefficients of straight chain ethyl esters was 13.4%, whereas the averaged relative increase in matrix-phase concentrations was 2.5%. Such a discrepancy in the effects of ascorbic acid between full-alcohol and low-alcohol matrices implies that ethanol may play an important role in regulating the antioxidant behavior of this compound. Indeed, Hsu and colleagues reported that the degradation rate of ascorbic acid conforms to first-order kinetics and is faster with elevated ethanol concentrations. For example, under the conditions most comparable to the current study (400 mg/L ascorbic acid, pH = 3.2, 25 °C storage temperature), the half-life of ascorbic acid was 9.69 days in 0% *v/v* hydroethanolic solutions and 7.76 days in 10% *v/v* counterparts.[58] The accelerated degradation of ascorbic, as well as that of catechin, due to increased ethanol content in an ascorbic acid/catechin solution (500 mg/L of each compound), was also reported by Chuang, Shen and Wu. This effect was ascribed to the lowered water activity in solutions with higher ethanol content, which favors the faster decomposition of dehydroascorbic acid and hence shifts the chemical equilibrium towards ascorbic acid degradation.[59] The current results reiterated the need to use ascorbic acid as a wine antioxidant with care.

Ethanol-dependent effects were also observed for copper. It can be seen from Figure 4 (A) and (C) that when either one of polyphenols or ascorbic acid, or both, was present in the matrix, the effect of copper on PPD became less pronounced in the 7% *v/v* alcohol environment compared to the 12% *v/v* counterpart. However, if neither antioxidant was present (configuration [C1, P0, A0]), the PPD values were much higher in the 7% *v/v* alcohol environment. FSO_2 analyses further indicated that the loss of free sulfur dioxide during oxidation was

consistently higher in matrices of 12% *v/v* alcohol than with 7% *v/v* alcohol, when copper was present, regardless of the presence or absence of either antioxidants. Although copper is a well-established catalyst of wine oxidation given its ability to accelerate the recycling of Fe(II)/Fe(III) redox pair,[26] evidence regarding the effect of ethanol content on the pro-antioxidant behavior of copper remains limited. Hence, future research is needed to further examine the relationship between copper as an oxidation catalyst and wine alcohol content.

In summary, in order to minimize the loss of gas-phase concentration of volatile esters in wine-like matrices during oxidation, the most effective antioxidant approach for full-alcohol (12% *v/v*) wines is to include polyphenols without ascorbic acid, whereas for low-alcohol (7% *v/v*) wines, both polyphenols and ascorbic acid can be beneficial. In each case, copper promotes oxidation and the loss of esters in the headspace in low-alcohol wines, but does not induce statistically significant ester loss in full-alcohol wines. These findings could aid winemakers to determine the best interventions in combating wine oxidation, especially during bulk liquid storage in tank or bulk transport, where large volumes of ullage and oxygen ingression may be present.

3.4.3 C/PPD of individual matrix components: decomposed simple effects analysis

When performing the ANOVA analyses to evaluate the impacts of matrix component additions, a top-down strategy was adopted, *i.e.*, the highest level (three-way) interactions between copper, polyphenols and ascorbic acid were identified first, and, if present, were decomposed into simple two-way interactions (altering two components while holding the other unaltered) and simple-simple main effects (altering one component while holding the other two unaltered). All three-way and two-way interactions for the ten esters are summarized in Table 4. Statistically significant three-way and two-way interactions were seen with all of the ten esters with a few exceptions. These included the three-way interaction for ethyl octanoate in full alcohol matrices and polyphenol × ascorbic acid two-way interaction for hexyl acetate in low alcohol matrices. These exceptions indicate that the effect of one component addition strongly depends on the presence or absence of other components in the system.

Table 4. Two-way and three-way interactions between copper (C), polyphenol (P) and ascorbic acid (A) on C/PPD of the ten volatile esters during 30-day oxidation in simulated wine matrices. Statistical significance values of these interactions are reported as follows: < 0.001, *; < 0.01, **; < 0.05, *; 0.05–0.1, numerical values; > 0.1, n.s.**

Compound	Full alcohol (12% *v/v*) matrices				Low alcohol (7% *v/v*) matrices			
	C × P	C × A	P × A	C × P × A	C × P	C × A	P × A	C × P × A
Methyl acetate	*n.s.*	**	*n.s.*	**	***	***	***	*n.s.*
Isobutyl acetate	***	***	***	***	***	***	***	***
Isoamyl acetate	***	***	***	***	*n.s.*	***	***	***
Hexyl acetate	***	***	***	***	*n.s.*	***	*n.s.*	***
Ethyl butyrate	***	***	***	***	***	***	***	***
Ethyl hexanoate	**	***	***	***	***	***	***	***
Ethyl octanoate	***	***	***	*n.s.*	***	***	***	***
Ethyl isobutyrate	***	***	***	***	***	***	***	***
Ethyl isovalerate	***	***	***	***	***	***	***	***
Ethyl 2-methylbutyrate	***	***	***	***	***	***	***	***

The fully decomposed addition impacts are visualized in Figure 5. As discussed in section 3.4.2, in the case of full-alcohol matrices, ascorbic acid mainly caused an increase in PPD values, whereas in low-alcohol matrices, ascorbic acid could effectively lower the partial pressure difference (groups 9–12).

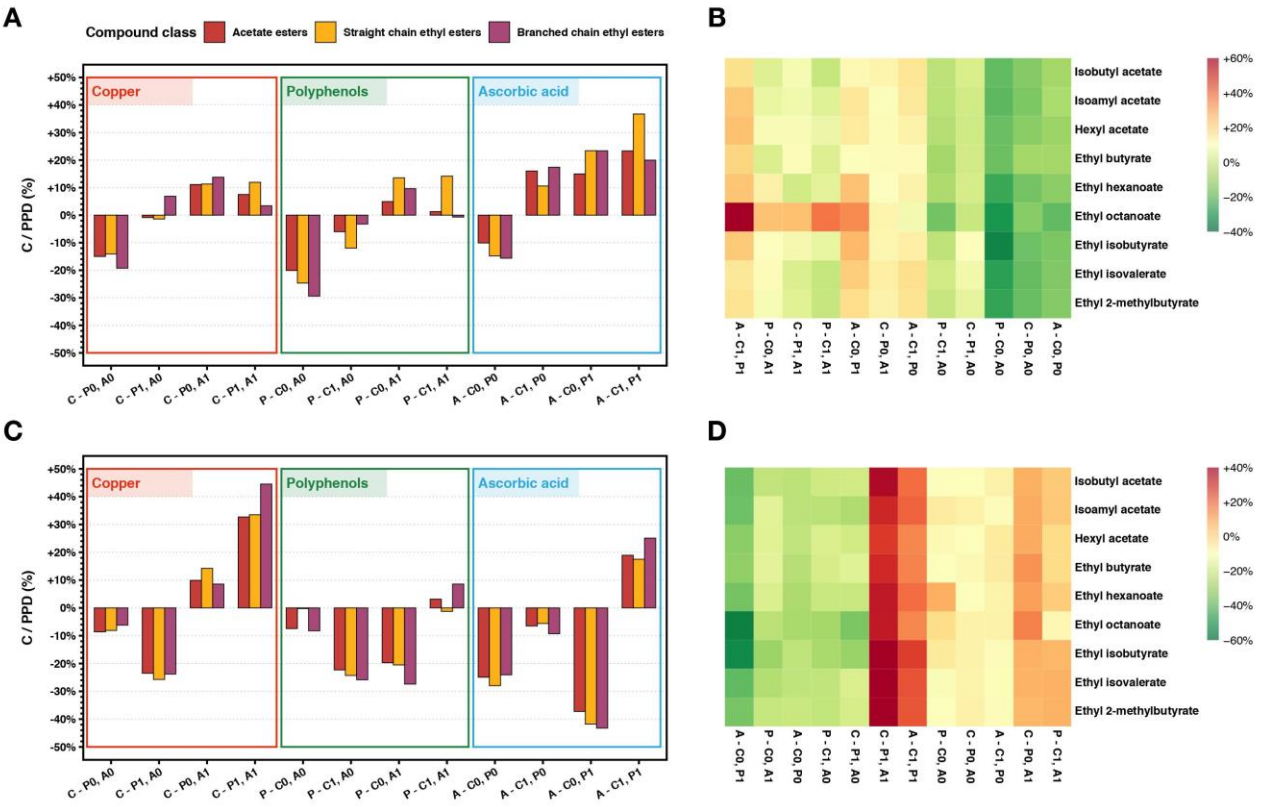

Figure 5. Effects of individual component additions on the changes of partial pressure difference (PPD) during 30-day oxidation in simulated wine matrices. The denotations of component effects are formatted as follows: X – Y0/1, Z0/1, where X indicates the component to be added, Y and Z indicates the other two components held constant, 0/1 indicates the absence/presence of the two constant component. For example, P - C1, A0 denotes the effect of adding polyphenols to the matrix on PPD values when the copper is present and ascorbic acid is absent. (A) and (B): effects of individual component additions on different volatile compound classes and on individual volatile compounds in full-alcohol (12% *v/v*) matrices. (C) and (D): effects of individual component additions on different volatile compound classes and on individual volatile compounds in low-alcohol (7% *v/v*) matrices. Note that the order of matrix components in heatmaps is sorted according to C/PPD effects similarity and are different from that shown in bar plots.

Similarly, the effects of polyphenol additions in decreasing PPD were also more pronounced in the low-alcohol matrices. Indeed, polyphenols may be added into reduced-alcohol white wine to re-balance body and fullness,[60] which is supported by the current results that indicate better protection against oxidative loss of aroma. In the full-alcohol matrices, on the other hand, adding polyphenols results in up to −30% C/PPD value, when neither copper nor ascorbic acid were in the matrix, which was the best protection against partial pressure loss amongst the eight polyphenols and ascorbic acid simple effects (groups 5–12, Figure 5 (A)). When ascorbic acid was present in the full-alcohol matrices, the use of polyphenols resulted in higher C/PPD values for ethyl octanoate and branched chain ethyl esters (see Figure 5 (B)). Under these particular settings, the changes in partition coefficients between pre- and post-oxidation were considerably modified by the involvement of polyphenols. For example, the partition coefficients of ethyl octanoate was 0.0243 and 0.0342 for configuration [C1, P0, A1] before and after oxidation, respectively. For configuration [C1, P1, A1], the partition coefficients were 0.0262 and 0.0149 before and after oxidation, respectively. One potential explanation for this phenomenon is synergistic effects between polyphenol oxidation products and ascorbic acid degradation products, which collectively enhanced the hydrophobicity of the matrix to retain hydrophobic aroma compounds. Nevertheless, future research is needed to investigate, preferably from a molecular level, the compounded effects of polyphenols and ascorbic acid on matrix hydrophobicity and resulting changes in volatiles.

Moreover, the use of copper showed a decrease in C/PPD values for both full-alcohol and low-alcohol matrices, especially when ascorbic acid was not involved (groups 1 and 2). Such effects were due to the increased partition coefficients of volatile esters, which offset their decline in matrix-phase concentrations, meaning that they mostly retained their partial pressure. Still, copper additions did indicate up to +48.4% C/PPD value for individual esters in the low-alcohol matrix with both polyphenols and ascorbic acid present, which points to a harmful loss of aroma in oxidized low-alcohol wines.

The current research explored the wine aroma from an innovative angle, *i.e.*, the partition coefficient and partial pressure. Contrary to traditional methods, where quantitation focuses on the total concentration of volatile compounds in the entire sample, partial pressure points to the sensorially relevant presence of volatiles in the headspace phase. Therefore, studying the changes in partial pressure of volatile compounds can directly highlight the loss of fruity perception after wine oxidation. The matrix component effects study also relates the partial pressure concept to different winemaking additions, such as the controversial use of ascorbic acid, for which a cross-over from antioxidant to pro-oxidant may occur in wine.[55] The combinatory application of ascorbic acid and sulfur dioxide has been previously reported as beneficial in boosting the concentration of polyfunctional mercaptans if added into grape must prior to alcoholic fermentation.[61] Results from the current study, however, highlighted that such treatment might lead to greater susceptibility towards oxidation in the finished wine should the added ascorbic acid remain post-fermentation. Additionally, these effects of matrix component combinations are of particular interest to winemakers, especially in bulk liquid handling, where oxygen ingress into the wine is happening. For example, Walther, Durner and Fischer reported the compromise of wine freshness during bulk transport, as characterized by the loss of several acetate and straight chain ethyl esters, comparable to the findings in the current study using commercial wines.[62] Hence, the idea of partial pressure could in the future help to deepen the understanding of the impact of oxidation on wine aroma and to establish effective countermeasures against oxidation.

Acknowledgements

The authors would like to express sincere gratitude towards Constellation Brands, NZ, who kindly supplied us with all the wine samples used in the current study. They also thank Dr. Melodie Lindsay for her help in the validatory work of wine oxidation compounds using HPLC. Lastly, they would like to thankfully acknowledge Callaghan Innovation for financial support (contract number: CONB1801).

Conflict of Interest

The authors declare no competing financial interest.

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

- Table S1. Spiking levels of volatile compounds used for the calculation of partial pressure in the matrix component effects study.
- Table S2. Estimations of physicochemical properties of the ten volatile esters.
- Table S3. Odor thresholds of the ten volatile esters and the matrices used for odor threshold determination.
- Table S4. Temperature dependence of partition coefficient of the ten volatile esters in white wine.
- Table S5. Additional oxidation-related parameters monitored during the 30-day oxidation process.
- Table S6. Free sulfur dioxide and total antioxidant capacity changes as effects of the 30-day oxidation process in simulated wine matrices.

- Figure S1. The effect of different incubation times on the signal intensities of selected volatile esters using SHS-GC-IMS.
- Figure S2. The effect of different injection rates on the intensities and morphology of selected volatile ester signals using SHS-GC-IMS.
- Figure S3. The linear relationship between partition coefficients and odor thresholds of straight chain and branched chain ethyl esters.
- Figure S4. Cube plots for nine volatile esters demonstrating the effects of matrix component combinations and the simple effects of single component additions on partial pressure changes during 30-day oxidation.

References

1. Kreitman, G. Y.; Laurie, V. F.; Elias, R. J., Investigation of ethyl radical quenching by phenolics and thiols in model wine. *J. Agric. Food Chem.* **2013,** *61* (3), 685-692.

2. Waterhouse, A. L.; Laurie, V. F., Oxidation of Wine Phenolics: A Critical Evaluation and Hypotheses. *Am. J. Enol. Vitic* **2006,** *57* (3), 306-313.

3. Escudero, A.; Cacho, J.; Ferreira, V., Isolation and identification of odorants generated in wine during its oxidation: a gas chromatography–olfactometric study. *Eur. Food Res. Technol.* **2000,** *211* (2), 105-110.

4. Peterson, A. L.; Gambuti, A.; Waterhouse, A. L., Rapid analysis of heterocyclic acetals in wine by stable isotope dilution gas chromatography–mass spectrometry. *Tetrahedron* **2015,** *71* (20), 3032-3038.

5. Nikolantonaki, M.; Chichuc, I.; Teissedre, P. L.; Darriet, P., Reactivity of volatile thiols with polyphenols in a wine-model medium: impact of oxygen, iron, and sulfur dioxide. *Anal. Chim. Acta* **2010,** *660* (1-2), 102-109.

6. Patrianakou, M.; Roussis, I. G., Decrease of Wine Volatile Aroma Esters by Oxidation. *S. Afr. J. Enol. Vitic.* **2013,** *34* (2), 241-245.

7. Ferreira, V.; Carrascon, V.; Bueno, M.; Ugliano, M.; Fernandez-Zurbano, P., Oxygen Consumption by Red Wines. Part I: Consumption Rates, Relationship with Chemical Composition, and Role of SO2. *J. Agric. Food Chem.* **2015,** *63* (51), 10928-10937.

8. Carrascón, V.; Bueno, M.; Fernandez-Zurbano, P.; Ferreira, V., Oxygen and SO2 Consumption Rates in White and Rose Wines: Relationship with and Effects on Wine Chemical Composition. *J. Agric. Food Chem.* **2017,** *65* (43), 9488-9495.

9. Kontoudakis, N.; Clark, A. C., Sulfide-binding to Cu(II) in wine: Impact on oxygen consumption rates. *Food Chem.* **2020,** *316*, 126352.

10. Nikolantonaki, M.; Waterhouse, A. L., A method to quantify quinone reaction rates with wine relevant nucleophiles: a key to the understanding of oxidative loss of varietal thiols. *J. Agric. Food Chem.* **2012,** *60* (34), 8484-8491.

11. Roussis, I. G.; Lambropoulos, I.; Papadopoulou, D., Inhibition of the decline of volatile esters and terpenols during oxidative storage of Muscat-white and Xinomavro-red wine by caffeic acid and N-acetyl-cysteine. *Food Chem.* **2005,** *93* (3), 485-492.

12. Makhotkina, O.; Kilmartin, P. A., Hydrolysis and formation of volatile esters in New Zealand Sauvignon blanc wine. *Food Chem.* **2012,** *135* (2), 486-493.

13. Zhu, W.; Benkwitz, F.; Sarmadi, B.; Kilmartin, P. A., Validation Study on the Simultaneous Quantitation of Multiple Wine Aroma Compounds with Static Headspace-Gas Chromatography-Ion Mobility Spectrometry. *J. Agric. Food Chem.* **2021,** *69* (49), 15020-15035.

14. Ettre, L. S.; Welter, C.; Kolb, B., Determination of Gas-Liquid Partition Coefficients by Automatic Equilibrium Headspace - Gas Chromatography Utilizing the Phase Ratio Variation Method. *Chromatographia* **1993,** *35* (1/2), 73-84.

15. Sander, R., Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.* **2015,** *15* (8), 4399-4981.

16. Robbins, G. A.; Wang, S.; Stuart, J. D., Using the static headspace method to determine Henry's law constants. *Anal. Chem.* **1993,** *65* (21), 3113-3118.

17. Lodge, K. B.; Danso, D., The measurement of fugacity and the Henry's law constant for volatile organic compounds containing chromophores. *Fluid Ph. Equilibria* **2007,** *253* (1), 74-79.

18. Jenkins, T. W.; Howe, P. A.; Sacks, G. L.; Waterhouse, A. L., Determination of Molecular and "Truly" Free Sulfur Dioxide in Wine: A Comparison of Headspace and Conventional Methods. *Am. J. Enol. Vitic.* **2020,** *71* (3), 222-230.

19. Kolb, B., Headspace Gas Chromatography. In *Encyclopedia of Separation Science*, 2000; pp 489-496.

20. Zhu, W.; Benkwitz, F.; Kilmartin, P. A., Volatile-Based Prediction of Sauvignon Blanc Quality Gradings with Static Headspace-Gas Chromatography-Ion Mobility Spectrometry (SHS-GC-IMS) and Interpretable Machine Learning Techniques. *J. Agric. Food Chem.* **2021,** *69* (10), 3255-3265.

21. Iland, P., *Chemical Analysis of grapes and wine*. Patrick Iland Wine Promotions, **2004**.

22. Paixão, N.; Perestrelo, R.; Marques, J. C.; Câmara, J. S., Relationship between antioxidant capacity and total phenolic content of red, rosé and white wines. *Food Chem.* **2007,** *105* (1), 204-214.

23. Baltrušaitytė, V.; Venskutonis, P. R.; Čeksterytė, V., Radical scavenging activity of different floral origin honey and beebread phenolic extracts. *Food Chem.* **2007,** *101* (2), 502-514.

24. Wollan, D.; Pham, D.-T.; Wilkinson, K. L., Changes in Wine Ethanol Content Due to Evaporation from Wine Glasses and Implications for Sensory Analysis. *J. Agric. Food Chem.* **2016,** *64* (40), 7569-7575.

25. Bradshaw, M. P.; Scollary, G. R.; Prenzler, P. D., Examination of the sulfur dioxide–ascorbic acid anti-oxidant system in a model white wine matrix. *J. Sci. Food Agric.* **2004,** *84* (4), 318-324.

26. Danilewicz, J. C., Review of Reaction Mechanisms of Oxygen and Proposed Intermediate Reduction Products in Wine: Central Role of Iron and Copper. *Am. J. Enol. Vitic* **2003,** *54* (2), 73-85.

27. Danilewicz, J. C., Role of tartaric and malic acids in wine oxidation. *J. Agric. Food Chem.* **2014,** *62* (22), 5149-5155.

28. Cameleyre, M.; Lytra, G.; Barbe, J.-C., Static Headspace Analysis Using Low-Pressure Gas Chromatography and Mass Spectrometry, Application to Determining Multiple Partition Coefficients: A Practical Tool for

744 Understanding Red Wine Fruity Volatile Perception and the Sensory Impact of Higher Alcohols. *Anal.*
745 *Chem.* **2018,** *90* (18), 10812-10818.

746 29. del Mar Contreras, M.; Arroyo-Manzanares, N.; Arce, C.; Arce, L., HS-GC-IMS and chemometric data
747 treatment for food authenticity assessment: Olive oil mapping and classification through two different
748 devices as an example. *Food Control* **2019,** *98*, 82-93.

749 30. Athès, V.; Peña y Lillo, M.; Bernard, C.; Pérez-Correa, R.; Souchon, I., Comparison of Experimental
750 Methods for Measuring Infinite Dilution Volatilities of Aroma Compounds in Water/Ethanol Mixtures. *J.*
751 *Agric. Food Chem.* **2004,** *52* (7), 2021-2027.

752 31. Martuscelli, M.; Savary, G.; Pittia, P.; Cayot, N., Vapour partition of aroma compounds in strawberry
753 flavoured custard cream and effect of fat content. *Food Chem.* **2008,** *108* (4), 1200-1207.

754 32. Cameleyre, M.; Monsant, C.; Tempere, S.; Lytra, G.; Barbe, J.-C., Toward a Better Understanding of
755 Perceptive Interactions between Volatile and Nonvolatile Compounds: The Case of Proanthocyanidic
756 Tannins and Red Wine Fruity Esters-Methodological, Sensory, and Physicochemical Approaches. *J. Agric.*
757 *Food Chem.* **2021,** *69* (34), 9895-9904.

758 33. Aznar, M.; Tsachaki, M.; Linforth, R. S. T.; Ferreira, V.; Taylor, A. J., Headspace analysis of volatile organic
759 compounds from ethanolic systems by direct APCI-MS. *Int. J. Mass Spectrom.* **2004,** *239* (1), 17-25.

760 34. Peyches-Bach, A.; Dombre, C.; Moutounet, M.; Peyron, S.; Chalier, P., Effect of ethanol on the sorption of
761 four targeted wine volatile compounds in a polyethylene film. *J. Agric. Food Chem.* **2012,** *60* (27), 6772-
762 6781.

763 35. Reichardt, C.; Welton, T., Properties, Purification, and Use of Organic Solvents. In *Solvents and Solvent*
764 *Effects in Organic Chemistry, Fourth Edition*, 2010; pp 549-586.

765 36. Robinson, A. L.; Ebeler, S. E.; Heymann, H.; Boss, P. K.; Solomon, P. S.; Trengove, R. D., Interactions
766 between wine volatile compounds and grape and wine matrix components influence aroma compound
767 headspace partitioning. *J. Agric. Food Chem.* **2009,** *57* (21), 10313-10322.

768 37. Tsachaki, M.; Gady, A.-L.; Kalopesas, M.; Linforth, R. S. T.; Athès, V.; Marin, M.; Taylor, A. J., Effect of
769 Ethanol, Temperature, and Gas Flow Rate on Volatile Release from Aqueous Solutions under Dynamic
770 Headspace Dilution Conditions. *J. Agric. Food Chem.* **2008,** *56* (13), 5308-5315.

771 38. Conner, J. M.; Birkmyre, L.; Paterson, A.; Piggott, J. R., Headspace concentrations of ethyl esters at
772 different alcoholic strengths. *J. Sci. Food Agric.* **1998,** *77* (1), 121-126.

773 39. Price, W. S.; Ide, H.; Arata, Y., Solution Dynamics in Aqueous Monohydric Alcohol Systems. *J. Phys. Chem.*
774 *A* **2003,** *107* (24), 4784-4789.

775 40. Abraham, M. H.; Gola, J. M. R.; Cometto-Muniz, J. E.; Cain, W. S., A model for odour thresholds. *Chem.*
776 *Senses* **2002,** *27* (2), 95-104.

41. Ammari, A.; Schroen, K., Effect of Ethanol and Temperature on Partition Coefficients of Ethyl Acetate, Isoamyl Acetate, and Isoamyl Alcohol: Instrumental and Predictive Investigation. *J. Chem. Eng. Data* **2019,** *64* (8), 3224-3230.

42. Muñoz-González, C.; Martín-Álvarez, P. J.; Moreno-Arribas, M. V.; Pozo-Bayón, M. Á., Impact of the nonvolatile wine matrix composition on the in vivo aroma release from wines. *J. Agric. Food Chem.* **2014,** *62* (1), 66-73.

43. Danilewicz, J. C.; Wallbridge, P. J., Further Studies on the Mechanism of Interaction of Polyphenols, Oxygen, and Sulfite in Wine. *Am. J. Enol. Vitic* **2010,** *61* (2), 166-175.

44. du Toit, W. J.; Marais, J.; Pretorius, I. S.; du Toit, M., Oxygen in Must and Wine: A review. *S. Afr. J. Enol. Vitic.* **2006,** *27* (1), 76-94.

45. Pati, S.; Crupi, P.; Benucci, I.; Antonacci, D.; Di Luccia, A.; Esti, M., HPLC-DAD–MS/MS characterization of phenolic compounds in white wine stored without added sulfite. *Food Res. Int.* **2014,** *66*, 207-215.

46. Mitropoulou, A.; Hatzidimitriou, E.; Paraskevopoulou, A., Aroma release of a model wine solution as influenced by the presence of non-volatile components. Effect of commercial tannin extracts, polysaccharides and artificial saliva. *Food Res. Int.* **2011,** *44* (5), 1561-1570.

47. Lorrain, B.; Tempere, S.; Iturmendi, N.; Moine, V.; de Revel, G.; Teissedre, P.-L., Influence of phenolic compounds on the sensorial perception and volatility of red wine esters in model solution: an insight at the molecular level. *Food Chem.* **2013,** *140* (1-2), 76-82.

48. Danilewicz, J. C.; Seccombe, J. T.; Whelan, J., Mechanism of Interaction of Polyphenols, Oxygen, and Sulfur Dioxide in Model Wine and Wine. *Am. J. Enol. Vitic.* **2008,** *59* (2), 128-136.

49. Makhotkina, O.; Kilmartin, P. A., Electrochemical oxidation of wine polyphenols in the presence of sulfur dioxide. *J. Agric. Food Chem.* **2013,** *61* (23), 5573-5581.

50. Audouin, V.; Bonnet, F.; Vickers, Z. M.; Reineccius, G. A., Limitations in the Use of Odor Activity Values to Determine Important Odorants in Foods. In *Gas Chromatography-Olfactometry: The State of the Art*, 2001; pp 156-171.

51. Benkwitz, F.; Nicolau, L.; Lund, C.; Beresford, M.; Wohlers, M.; Kilmartin, P. A., Evaluation of key odorants in sauvignon blanc wines using three different methodologies. *J. Agric. Food Chem.* **2012,** *60* (25), 6293-6302.

52. Coetzee, C.; Van Wyngaard, E.; Šuklje, K.; Ferreira, A. C. S.; du Toit, W. J., Chemical and Sensory Study on the Evolution of Aromatic and Nonaromatic Compounds during the Progressive Oxidative Storage of a Sauvignon blanc Wine. *J. Agric. Food Chem.* **2016,** *64* (42), 7979-7993.

53. Coetzee, C.; du Toit, W. J., Sauvignon blanc wine: Contribution of ageing and oxygen on aromatic and non-aromatic compounds and sensory composition - A review. *S. Afr. J. Enol. Vitic.* **2015,** *36* (3), 347-365.

54. Escudero, A.; Asensio, E.; Cacho, J.; Ferreira, V., Sensory and chemical changes of young white wines stored under oxygen. An assessment of the role played by aldehydes and some other important odorants. *Food Chem.* **2002,** *77* (3), 325-331.

55. Barril, C.; Rutledge, D. N.; Scollary, G. R.; Clark, A. C., Ascorbic acid and white wine production: a review of beneficial versus detrimental impacts. *Aust. J. Grape Wine Res.* **2016,** *22* (2), 169-181.

56. Clark, A. C.; Grant-Preece, P.; Cleghorn, N.; Scollary, G. R., Copper(II) addition to white wines containing hydrogen sulfide: residual copper concentration and activity. *Aust. J. Grape Wine Res.* **2015,** *21* (1), 30-39.

57. Lund, C. M.; Nicolau, L.; Gardner, R. C.; Kilmartin, P. A., Effect of polyphenols on the perception of key aroma compounds from Sauvignon Blanc wine. *Aust. J. Grape Wine Res.* **2009,** *15* (1), 18-26.

58. Hsu, H.-Y.; Tsai, Y.-C.; Fu, C.-C.; Wu, J. S.-B., Degradation of ascorbic acid in ethanolic solutions. *J. Agric. Food Chem.* **2012,** *60* (42), 10696-10701.

59. Chuang, P.-T.; Shen, S.-C.; Wu, J. S.-B., Browning in ethanolic solutions of ascorbic acid and catechin. *J. Agric. Food Chem.* **2011,** *59* (14), 7818-7824.

60. Schmitt, M.; Christmann, M., Dealcoholization of white wines. In *White Wine Technology*, 2022; pp 369-377.

61. Lyu, X.; Araújo, L. D.; Quek, S.-Y.; Kilmartin, P. A., Effects of Antioxidant and Elemental Sulfur Additions at Crushing on Aroma Profiles of Pinot Gris, Chardonnay and Sauvignon Blanc Wines. *Food Chem.* **2021,** *346*, 128914.

62. Walther, A.-K.; Durner, D.; Fischer, U., Impact of Temperature during Bulk Shipping on the Chemical Composition and Sensory Profile of a Chardonnay Wine. *Am. J. Enol. Vitic.* **2018,** *69* (3), 247-257.