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Impact of microoxygenation on Pinot noir wines with different initial phenolic content

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ABSTRACT

Microoxygenation (MOX) is used to improve wine colour and sensory quality; however, limited information is available for Pinot noir wines and wines with different initial phenolic content. In this study, MOX was applied to two Pinot noir wines, with either a low or a high phenolic content, at two doses (0.50 and 2.11 mg/L/day) for 14 days. With the sterile filtration applied, acetaldehyde formation during MOX was very low, supporting the influence of yeast on acetaldehyde production during MOX. The MOX dosage rate did not significantly affect colour development, while the Pinot noir wine with higher phenolics benefited from MOX to a greater extent, significantly increasing colour intensity and SO_2 resistant (polymeric) pigments. However, these changes did not guarantee colour stability, as a final SO_2 addition (100 mg/L) largely erased the MOX induced colour improvements in all wines. This could be due to the lower acetaldehyde formation, thus less ethyl-bridged stable pigments resistant to SO_2 bleaching. MOX also decreased the flavan-3-ols and anthocyanin monomers, which differed between the two Pinot noir wines, reflecting the initial phenolic content. Lastly, MOX generally increased the measured tannin concentration and affected the proportion of tannin subunits, with a decrease in tannin mass conversion and proportion of (-)-epigallocatechin extension units. Some of these changes in phenolic compounds could potentially increase astringency, suggesting that MOX should be applied to Pinot noir and other low phenolic wines with caution.

KEYWORDS

microoxygenation, initial phenolics, colour development, monomeric phenolics, tannin composition, Pinot noir

Supplementary data can be downloaded through: https://oeno-one.eu/article/view/4840

INTRODUCTION

Over the years, microoxygenation (MOX) has become a popular vinification technique to mimic barrel ageing and enhance wine sensory qualities. These improvements include wine colour stabilisation, softening of astringency, and reducing vegetal characteristics (Cejudo-Bastante *et al.,* 2012; Schmidtke *et al.,* 2011). Several factors affecting the influence of MOX on red table wines have been demonstrated, such as the timing and duration of MOX, the addition of preservatives, oxygen dosage, and microbial influence (Anli and Cavuldak, 2012; Ji *et al.,* 2020). However, very limited information is available for wines made from Pinot noir (Durner *et al.,* 2010; Durner *et al.,* 2015; Yang *et al.,* 2021a; Yang *et al.,* 2021b). Pinot noir wines tend to be lighter in colour than Cabernet-Sauvignon, Malbec and Syrah wines (Burns and Osborne, 2013; Casassa *et al.,* 2015) and are associated with poor colour development, low pigment stability, and limited ageing potential (Sacchi *et al.,* 2005; Sparrow *et al.,* 2016). Therefore, MOX could potentially be an important tool in Pinot noir winemaking to improve wine colour.

Recently, we have demonstrated that MOX applied to a young Pinot noir wine led to an increase in colour intensity (with a higher absorbance at 520 nm) and tannin concentration, and a higher oxygen dosage favoured the formation of polymeric pigments (Yang *et al.,* 2021a; Yang *et al.,* 2021b). At the same time, a higher percentage of galloylated tannins but fewer trihydroxylated tannins were found after MOX, indicating a negative impact on astringency perceptions (Yang *et al.,* 2021a; Yang *et al.,* 2021b). However, Yang *et al.* (2021b), attributed the decrease in trihydroxylated tannins to *Saccharomyces cerevisiae* activity, as MOX had also induced yeast growth (Yang *et al.,* 2021a), where the proliferation and autolysis of this yeast species have been shown to affect tannin composition through adsorption to the cell walls (Mazauric and Salmon, 2005; Mekoue Nguela *et al.,* 2015). Therefore, the changes in tannin composition observed in previous work (Yang *et al.,* 2021b) might not be solely caused by oxygenation. Nevertheless, it has been suggested that the oxidation of wines that have few free anthocyanins can lead to extensive tannin polymerisation, resulting in a dryness sensation (Boulton, 2001; Gómez-Plaza and Cano-López, 2011; Oberholster *et al.,* 2015). This possibility to increase the astringency could be a cause for concern when applying MOX to Pinot noir wines.

Cano-López *et al.* (2008) reported that MOX applied to Monastrell wines with high initial phenolic contents, and particularly high anthocyanin concentrations (i.e., approximately 450 to 550 mg/L), resulted in a greater formation of anthocyanin-derived pigments and colour intensity, along with a decrease in the mean degree of polymerisation (mDP) of tannins. By contrast, in wines with the lowest initial phenolic content and anthocyanin concentration (i.e., approximately 360 mg/L), MOX did not induce any significant change in colour development but increased the mDP value, suggesting a possible outcome of over-oxygenation. Besides Cano-López *et al.* (2008), no other report has been made on the influence of initial phenolic content on red wines undergoing MOX.

However, even the lowest phenolic concentration examined by Cano-López *et al.* (2008) may be considered high for Pinot noir wines. Cliff *et al.* (2007) surveyed 173 commercial red wines to find Pinot noir (n = 59) anthocyanin concentration was the lowest with an average of 61 mg/L (malvidin-3-glucoside equivalents). Another survey of 1350 commercial red wines found Pinot noir (n = 261) contained the lowest tannin concentration with an average of 348 ± 200 mg/L (catechin equivalents using the BSA tannin assay), which was only about half the concentration found in Cabernet-Sauvignon, Zinfandel and Merlot (Harbertson *et al.,* 2008).

Therefore, the present study was conducted to evaluate the MOX impact on Pinot noir wines with different phenolic content. This study involves two Pinot noir wines with a low (PN1) and a high (PN2) phenolic content and MOX was applied after malolactic fermentation and at two oxygen dosage rates for 14 days. To examine the pure chemical effects from MOX, the wines were sterile filtered to avoid microbial interference. The evolution of colour parameters, anthocyanins, polymeric pigments, monomeric phenolics and tannin composition are reported.

MATERIALS AND METHODS

1. Pinot noir wines

Two *Vitis vinifera* L. cv. Pinot noir wines (100 %) from the 2020 vintage, differing in their phenolic content (i.e., PN1 and PN2), were obtained from the Delegat Estate Winery, Blenheim, New Zealand.

TABLE 1. Wine composition and phenolic content of PN1 and PN2 wines at time 0 prior to starting MOX.

Initial Phenolic	Conventional Analyses							
Content	pH	TA	Malic Acid (g/L)	D-Glucose (g/L)	D-Fructose (g/L)	ALC %	Free SO_2 (mg/L)	Total SO_2 (mg/L)
Pinot noir 1 (PN1)	3.6 ± 0.0	7.8 ± 0.0	0.8 ± 0.0	0.4 ± 0.0	0.7 ± 0.1	14.3 ± 0.0	ND	36.0 ± 4.0
Pinot noir 2 (PN2)	3.6 ± 0.0	7.9 ± 0.0	0.6 ± 0.0	0.4 ± 0.1	2.0 ± 0.1	14.9 ± 0.0	ND	42.5 ± 2.5

Initial Phenolic	Harbertson-Adams assay			Tannins by Precipitation	T/A Ratio	Colour Absorbances				
Content	Total Anthocyanins (mg/L)	SPP (AU)	LPP (AU)	MCP Tannin (g/L)		420 nm	520 nm	Monomeric Anthocyanins	Colour Density	SO_2 Resistant Pigments
Pinot noir 1 (PN1)	191.8 ± 3.1	1.15 ± 0.02	0.04 ± 0.02	0.45 ± 0.01	2.3 ± 0.0	2.06 ± 0.01	3.59 ± 0.00	10.60 ± 0.10	5.65 ± 0.00	1.37 ± 0.00
Pinot noir 2 (PN2)	281.6 ± 2.3	1.40 ± 0.03	0.10 ± 0.01	0.67 ± 0.01	2.4 ± 0.0	2.62 ± 0.01	4.58 ± 0.00	16.66 ± 0.10	7.20 ± 0.00	1.54 ± 0.00

Initial values are presented as mean ± standard error for conventional analyses (n = 2) and phenolic analyses (n = 6); ALC%: wine alcohol content; SPP (AU): small polymeric pigments in absorbance unit at 520 nm; LPP (AU): large polymeric pigments in absorbance unit at 520 nm; MCP Tannin: tannin concentration measured by tannin precipitation with methylcellulose (Mercurio *et al.*, 2007); T/A Ratio: MCP tannin / total anthocyanins; ND: not detected.

The Pinot noir grapes came from the same vineyard, from own-rooted Pinot noir vines Entav INRA 667 under the Smart-Dyson trellis system and were crushed and destemmed, while PN2 received the free-run juice that was drained from the skins to produce the commercial wines. Commercial *Saccharomyces cerevisiae* yeast (Lalvin RC212™, Lallemand Oenology, Blagnac, France) was inoculated for primary fermentation, in which both wines took 16 days to complete with temperature control at 26 °C. Both wines had also spontaneously completed malolactic fermentation (uncontrolled due to COVID-19 lockdown) before skins pressing. Basic parameters for PN1 and PN2 upon MOX treatments are presented in Table 1. Besides the variations in phenolic content, a slightly higher alcohol content and fructose level were also found in the PN2 wine (Table 1).

2. MOX Trial

The set-up for MOX and control treatments were the same as outlined by Yang *et al.* (2021a). The control treatment received no oxygenation and was sealed in the 2 L Fisherbrand™ glass bottles. MOX treatments were carried out in 15 L stainless steel tanks and applied through a sealed-end diffuser tube, rolled up into a circular shape (r = 8.1 cm), with the fluorinated ethylene-propylene copolymer (FEP) membrane coating (TSFE14-0250-047-50, CHEMFLUOR®, Saint-Gobain Performance Plastics, Courbevoie, France) to introduce the microlevels of oxygen (food grade, BOC Gas, Auckland, New Zealand) into the wines. The diffusion of oxygen (food grade, BOC Gas, New Zealand) in each MOX tank was controlled using 2-stage primary oxygen regulators (BOC-8000) and high precision line regulators (BOC BS1-000-1700-N). The dissolved oxygen (DO) levels were measured non-intrusively using the PSt3 oxygen sensor (Vinventions, CA, USA).

Each control and MOX treatment were carried out in triplicate. Two different oxygen doses: 0.50 ± 0.08 and 2.11 ± 0.3 mg/L/day of O_2 were applied to both PN1 and PN2 for 14 days with temperature control at 15 ± 1 °C. Treatments are labelled as follows: MOX applied at 0.50 and 2.11 mg/L/day on Pinot noir wines with the low phenolic content (T1 and T2) and the control (C1); and with the high phenolic content (T3 and T4) and the control (C2). The two oxygenation rates were determined in a preliminary study using a 12 % ethanol solution, where oxygenation was applied at a pressure of 200 kPa and 500 kPa, respectively, for 120 hours. Without an external oxygen supply, the oxygen ingress into the MOX tanks was 1.17 ± 0.46 mg/L/month. Prior to oxygenation, the wines were sterile filtered at 0.20 µm pore size (Sartopore 2 Midicap, Göttingen, Germany). After MOX, the wines were aged for 1 month at 15 °C and followed by 100 mg/L addition of potassium metabisulfite (Enartis Winy, Italy). The endpoint was determined 4 days after SO_2 addition.

3. Wine sampling

The sampling method was as described by Yang *et al.* (2021a). Colour parameters and polymeric pigment content were measured at the beginning of the experiment (time 0), day 5, day 14 (end of MOX), day 44 (after MOX and ageing for 1 month, i.e., before SO_2 addition) and day 48 (the endpoint). For phenolic composition, the samples were taken and analysed at time 0, day 44 and day 48. We had to skip the phenolic analyses on day 14 due to the unprecedented COVID-19 lockdown in New Zealand.

4. Conventional analyses

Wine pH and TA were measured using an automatic wine titrator (Hanna Instruments®, Woonsocket, RI, USA). A photometric measurement was used to determine free and total SO_2, residual sugars (i.e., glucose and fructose), malic acid, acetaldehyde concentrations using enzymatic test kits from Megazyme (Bray, Ireland). For these analyses, a Thermo Spectronic Helios Gamma 9423 UV-vis spectrophotometer (Waltham, MA, USA) was used and absorbances were measured using visible cuvettes with a 2 mm path length (Mediray, Auckland, New Zealand). The alcohol content was measured using an Anton-Paar Alcolyzer (Graz, Austria).

5. Spectrophotometric analyses

Wine colour parameters including the absorbance of 420 nm and 520 nm, SO_2 resistant pigments, colour intensity, monomeric anthocyanins were determined using the methods described by Iland *et al.* (2013). Total anthocyanins (i.e., malvidin-3-glucoside equivalents mg/L), small and large polymeric pigments (i.e., SPP and LPP in absorbance units) were determined using the Harbertson-Adams assay (Harbertson *et al.,* 2003), with the reaction volumes adapted from Heredia *et al.* (2006).

6. High-performance liquid chromatography analysis of monomeric phenolics

Monomeric phenolic compounds were determined using the high-performance liquid chromatography (HPLC) method as described by Yang *et al.* (2021a). In brief, approximately 1.5 mL of wine was filtered through a 0.45 µm membrane filters (MicroScience, Auckland, New Zealand), of which 20 µL was injected into a reversed-phased C18 column (Kinetex C18, 2.6 µm, 100 Å, 100 mm × 4.6 mm) on an Agilent Technologies (Santa Clara, CA, USA) 1200 series HPLC system. A G1315D diode array detector was used and chromatograms were obtained at 280 nm (for flavan-3-ols), 320 nm (for hydroxycinnamic acids), 360 nm (for flavonols), and 520 nm (for free anthocyanins).

For the quantifications, external standards were used: gallic acid, (−)-epicatechin, (+)-catechin, vanillic acid, syringic acid, caffeic acid, *p*-coumaric acid, ferulic acid, t-resveratrol, rutin and malvidin-3-glucoside. The measurements of quercetin, quercetin-3-O-glucuronide, quercetin-3-glucoside are expressed as rutin equivalents (mg/L). The concentrations of *trans*- and *cis*-coutaric acids are expressed as p-coumaric acid equivalents (mg/L). The content of trans-caftaric acid was calculated as caffeic acid equivalents (mg/L). The limit of detection (LOD) and limit of quantitation (LOQ) were calculated based on a signal-to-noise ratio of 3:1 and 10:1, respectively.

7. Tannin concentration and extraction method

Tannin concentration was measured using the revised version of methylcellulose tannin precipitation assay (MCP tannins, epicatechin equivalents (ECE) g/L) as detailed by Mercurio *et al.* (2007). The extraction of tannin for the phloroglucinolysis reaction was carried out as described by Yang *et al.* (2021b) based on the methods of Jeffery *et al.* (2008) and of Kassara and Kennedy (2011). After purification and drying, the tannin extracts were reconstituted to 10 g/L with pure methanol (HPLC grade), according to the MCP tannin concentration of wines. The methanolic extracts were then immediately analysed or kept in a –80 °C freezer until analysis. For each treatment, two extractions were undertaken for each vessel (i.e., 6 replications for each treatment).

8. High-performance liquid chromatography analyses of tannins

Tannin composition was analysed via the acid-catalysed depolymerisation reaction of tannins in the presence of excess phloroglucinol (Kennedy and Jones, 2001). For detection, the same HPLC system and the C18 column as for the analysis of monomeric phenolics were used, and the chromatograms were monitored at 280, 360, 520 and 620 nm, with 280 nm as the main detecting wavelength. Methods for the phloroglucinolysis reaction and the HPLC runtimes and mobile phases were as described in Yang *et al.* (2021b). The injection volume was 20 µL and the column was held at 30 °C. The solvents used were: solvent A, 0.1 % formic acid in Milli-Q water (v/v); and solvent B, 0.1 % formic acid in acetonitrile (v/v). The elution conditions were as follows: 0 min (95 % solvent A, 5 % solvent B); 3.08 min (95 % solvent A, 5 % solvent B); 9.23 min (80 % solvent A, 20 % solvent B); 16.92 min (60 % solvent A, 40 % solvent B); 18.64 min (10 % solvent A, 90 % solvent B); 21.54 min (10 % solvent A, 90 % solvent B); and 23 min (95 % solvent A, 5 % solvent B) with an additional 7 min post-run. The flow rate was 1.3 mL/min.

An external standard calibration curve was established using (−)-epicatechin, based on the peak area of the pure compound at 280 nm. The proportions of tannin subunits (%) were calculated based on their concentrations expressed as (−)-epicatechin equivalents (in moles). The mean degree of polymerisation (mDP) and the tannin mass conversion (yield %) were calculated according to Kennedy and Jones (2001). The mDP was calculated using the sum of all tannin subunits divided by the sum of all terminal units. The tannin yield (%) was determined by using the total mass of all tannin subunits (in grams), which excluded the phloroglucinol portion of the adducts, divided by the concentration of tannins (i.e., 10 g/L) used for the analysis. The degree of tannin galloylation (i.e., seed tannin indicator) was the sum of (−)-epicatechin-3-O-gallate subunits (i.e., both the extension and terminal units), and the degree of trihydroxylation (i.e., skin tannin indicator) was the (−)-epigallocatechin extension units (%).

9. Microbial analysis

The effectiveness of the sterile filtration was evaluated during the experiment, where the samples were plated for microbial growth at time 0 (after filtration) and following the MOX treatments at days 5, 10, 44 and 48.

Prior to plating, a 10 µL aliquot of the undiluted and stained sample with methylene blue was dispensed into a haemocytometer slide and examined under a microscope. For the control treatments, microbial analyses were determined at time 0, day 44 and day 48. The details of the method were as described in Yang *et al.* (2021a). In brief, samples were plated on Wallerstein Laboratory Nutrient (WLN) medium for yeast, and 50 % de Man, Rogosa, and Sharpe (MRS) medium (with the addition of 25 mg/L natamycin) for bacterial quantification. This was followed by a 7-day incubation at 28 °C, before determination.

10. Chemicals and reagents

All chemical reagents were of the highest available analytical grade quality and purchased from Merck (Castle Hill, NSW, Australia) unless specifically noted. Biological reagents and agar mediums for microbial analyses are purchased from Merck (Castle Hill, NSW, Australia). Total and frees sulfite assay kit (K-SULPH), D-fructose/D-glucose assay kit (K-FRUGL), L-malic acid assay kit (K-LMAL-116A), and acetaldehyde assay kit (K-ACHYD) were purchased from Megazyme (Bray, Ireland). Milli-Q water was obtained from a Thermo Scientific Barnstead Nanopure water purification system. Bovine serum albumin was purchased from pHScientific (Auckland, New Zealand).

11. Statistical Analysis

Statistical analyses were performed with R Studio version 1.2.5033 (R version 4.0.3, Inc., Boston, MA, USA) and graphs were produced using Excel 2019 (Microsoft, Redmond, WA, USA). Tukey's honestly significant difference (HSD) test was used as a comparison test when the samples were significantly different after the analysis of variance (ANOVA), where raw p values < 0.05 were considered significant. For each analysis, quantitative data of each treatment are calculated as means of six values (i.e., 3 experimental replicates × 2 analytical replicates).

RESULTS AND DISCUSSION

1. Dissolved oxygen, acetaldehyde concentration and basic wine composition

The dissolved oxygen (DO) concentrations detected in the control and MOX treatments during the experiment are shown in Figure 1. On the last day of MOX (day 14), T2 and T4 had approximately 4 times higher DO concentrations than T1 and T3, respectively, in accordance with the higher oxygenation rate. During ageing, from day 15 to 32, DO was not monitored in T1 and T2 due to the COVID19-lockdown. After 1 month of ageing and before SO_2 addition (day 44), the remaining DO concentrations in T1 (0.7 ± 0.5 mg/L), T2 (2.3 ± 0.4 mg/L), T3 (1.1 ± 0.3 mg/L) and T4 (1.4 ± 0.7 mg/L) indicated a lower DO consumption rate than DO accumulations, which might also be associated with the oxygen ingress through the MOX tanks. At the endpoint, i.e., 4 days after SO_2 addition, the DO concentrations in wines with MOX remained similar to that observed at day 44, showing the lack of reactivity of SO_2 directly with oxygen (Danilewicz, 2003).

In previous MOX studies, a correlation between acetaldehyde production and the growth of *Saccharomyces cerevisiae* has been found (Sáenz-Navajas *et al.,* 2018; Ji *et al.,* 2020). It is known that *Saccharomyces cerevisiae* uses ethanol as a carbon source, when fermentable sugar becomes limited, which produces acetaldehyde (Galdieri *et al.,* 2010; Pozo-Bayón and Moreno-Arribas, 2011). During the present study, no cells or viable growth of *Saccharomyces cerevisiae* were detected in any of the treatments, confirming the effectiveness of the sterile filtration. Free SO_2 was not detected upon the application of MOX (Table 1). Therefore, any impact on the wine can thus be ascribed to purely chemical oxidation phenomena.

The conventional analyses carried out at the endpoint are presented in Table 2. In both PN1 and PN2, the results did not show any clear impact of the MOX treatments. During MOX, a small but apparent increase of acetaldehyde (close to 2 folds) was seen with the higher oxygen dosage at day 5 (Table 2), from c. 4.7 to 8.4 mg/L in T2 and 6.3 to 10.4 mg/L in T4. This can be associated with the chemical oxidation of ethanol, due to H_2O_2 released from phenolic oxidation and catalysed by the redox cycling of Fe (II) and Fe (III) (Wildenradt and Singleton, 1974; Ribéreau-Gayon *et al.,* 1983; Danilewicz, 2016).

Regarding the lower oxygen dosage, T3 had a similar acetaldehyde concentration as to C2 at the same time points, while a clear increase of T1 over C1 was observed by day 14. Cacho *et al.* (1995) found that acetaldehyde production from oxidation was affected by iron levels, in which the higher the iron concentration, the lower the increase in acetaldehyde content. This might be another influential factor between PN1 and PN2. Regardless, the total increase of

TABLE 2. Acetaldehyde concentrations in PN1 and PN2 with and without MOX and final wine composition at day 48.

Treatments		Pinot noir 1 (PN1)			Pinot noir 2 (PN2)		
MOX Dosage		No MOX (C1 & C2), Low MOX (T1 & T3) at 0.50 ± 0.08, & High MOX (T2 &T4) at 2.17 ± 0.3 mg/L/day of O_2					
Days		C1	T1	T2	C2	T3	T4
Time 0	Acetaldehyde (mg/L)	4.3 ± 0.0 a	4.4 ± 0.1 a	4.7 ± 0.0 a	5.4 ± 0.9 a	5.3 ± 0.7 a	6.3 ± 1.7 a
Day 5		NA	4.2 ± 0.1 c	8.4 ± 0.1 ab	NA	6.9 ± 0.3 bc	10.4 ± 1.3 a
Day 10		NA	4.6 ± 0.5 b	10.8 ± 0.1 a	NA	6.1 ± 0.5 b	10.3 ± 1.6 a
Day 14		4.6 ± 1.4 b	7.1 ± 1.1 b	11.5 ± 1.3 a	6.3 ± 0.6 b	6.1 ± 0.5 b	8.0 ± 1.0 ab
Day 44: after MOX and ageing for 30 days		4.6 ± 1.4 c	8.1 ± 1.4 b	8.2 ± 1.0 b	6.9 ± 0.5 bc	6.9 ± 0.8 bc	11.3 ± 1.5 a
100 mg/L potassium metabisulfite addition at day 44							
Day 48: end point analyses after SO_2 addition	Acetaldehyde (mg/L)	3.9 ± 0.1 c	8.1 ± 0.2 a	7.3 ± 0.7 ab	6.4 ± 0.4 b	5.8 ± 0.4 b	11.0 ± 2.4 a
	pH	3.6 ± 0.0 a	3.5 ± 0.0 a	3.5 ± 0.0 a	3.5 ± 0.0 a	3.5 ± 0.0 a	3.6 ± 0.0 a
	TA	7.7 ± 0.0 a	7.7 ± 0.0 a	7.7 ± 0.0 a	7.7 ± 0.0 a	7.8 ± 0.0 a	7.8 ± 0.0 a
	ALC %	14.3 ± 0.0 a	14.3 ± 0.0 a	14.3 ± 0.0 a	14.9 ± 0.0 b	14.9 ± 0.0 b	14.9 ± 0.0 b
	Free SO_2 (mg/L)	33.4 ± 1.7 a	34.8 ± 1.2 a	28.8 ± 4.2 ab	31.5 ± 1.7 a	24.5 ± 3.5 b	28.5 ± 1.5 ab
	Total SO_2 (mg/L)	83.5 ± 5.3 a	81.5 ± 4.5 a	85.7 ± 5.7 a	88.9 ± 3.6 a	86.5 ± 0.7 a	87.5 ± 2.6 a

Values are presented as mean ± standard error (n = 6); DO: dissolved oxygen; ALC%: wine alcohol content; NA, not available. Means within a row followed by different letters are significantly different (Tukey $p < 0.05$).

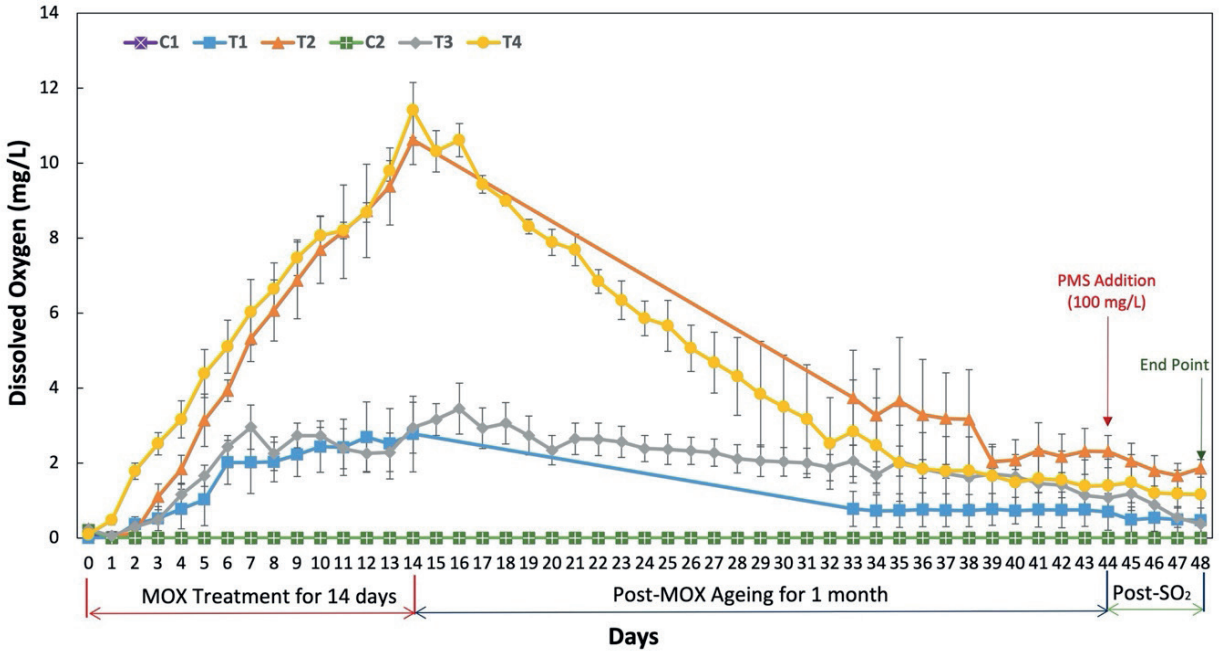

FIGURE 1. The concentration of DO monitored in different treatments during this experiment. Note the missing data in C1, T1 and T2 was due to the COVID-19 lockdown.

acetaldehyde in these wines was very limited compared to previous MOX studies where the growth of *Saccharomyces cerevisiae* was also observed (Sáenz-Navajas *et al.,* 2018; Ji *et al.,* 2020; Yang *et al.,* 2021a). In both Sáenz-Navajas *et al.* (2018), with oxygenation applied at 15 mg/L/month for 48 days, and Ji *et al.* (2020), with DO consumption at approximately 0.5 mg/L/day within 49 days, MOX treatments induced an increase of yeast growth to 10^5 CFU/mL towards the end of MOX, which coincided with the increase of acetaldehyde (c. 30–35 mg/L) and the depletion of free SO_2 and DO. Yang *et al.* (2021a), applied MOX both before and after MLF (10.8 and 52.4 mg/L/month for 30 days) and increased acetaldehyde (from around 55 to 120 mg/L, and 35 to 70 mg/L, respectively) at the beginning of treatments, where free SO_2 was not readily detected and DO was still climbing. The authors indicated the influence of dormant yeast and yeast lees on acetaldehyde production (Yang *et al.,* 2021a). From these previous studies, it also appeared that with MOX, the timing of acetaldehyde production could also be affected by the presence of free SO_2 that is not only known to bind acetaldehyde (Peterson and Waterhouse, 2016) but also can suppress yeast activity (Divol *et al.,* 2012). In the present trial, the low acetaldehyde increase supports the idea that the larger increases in acetaldehyde observed during past MOX trials can be associated with residual yeast activity.

2. Colour parameters and polymeric pigment content

During the experiment, an important increase in the 420 nm (Figure 2a) and 520 nm (Figure 2b) absorbances and colour intensity (Figure 2c) was observed in all treatments. On day 44, MOX treatments applied to PN2 (T3 and T4) showed significantly higher increases on these colour parameters, which were not significantly affected by the different MOX dosages. In PN1, significant increases were only found in T2 with the higher oxygen dosage ($p < 0.05$, Table S1, supporting information), but smaller compared to T3 and T4. Similar observations were found in the absorbance of SO_2 resistant pigments at 520 nm in T2, T3 and T4 (Figure 2d).

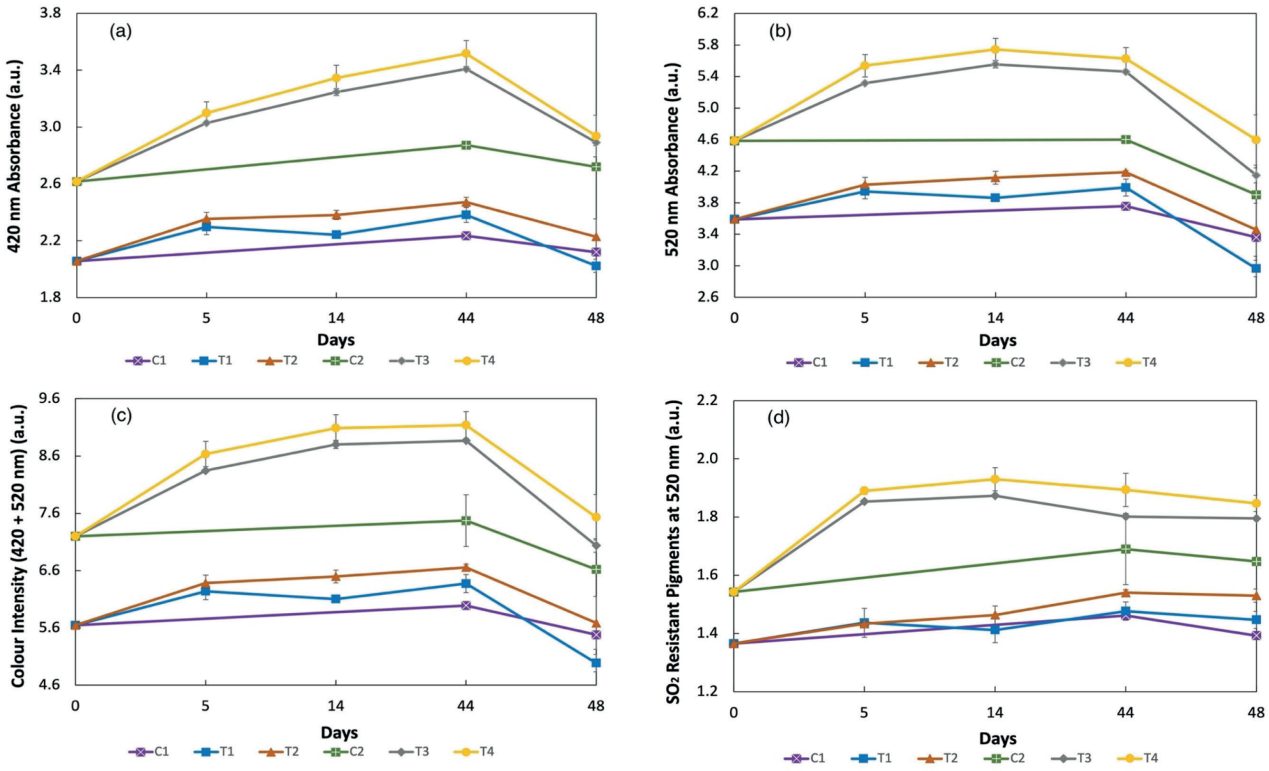

FIGURE 2. Effect of MOX at 0.50 and 2.11 mg/L/day for 14 days on Pinot noir wines with a low phenolic content (T1 and T2) and a high phenolic content (T3 and T4) compared to the controls (C1 and C2, respectively) on the change of colour absorbance by spectrophotometric measures at (a) 420 nm, (b) 520 nm, (c) colour intensity (420 + 520 nm), and (d) SO_2 resistant pigments at 520 nm (mean + standard error, n = 6).

These occurred with an induced decline in anthocyanins, where the decrease of monomeric anthocyanins (Figure 3a) and total anthocyanins (Figure 3b) in T3 (10 % and 10 %, respectively) and T4 (17 % and 13 %, respectively) was considerably higher than in T1 (3 % and 6 %, respectively) and T2 (5 % and 7 %, respectively). The higher decrease of anthocyanins, but increase in colour parameters in Pinot noir wine due to MOX, has been reported in Durner *et al.* (2010) and Yang *et al.* (2021a) as well as in other red wine varieties (Anli and Cavuldak, 2012). Here, the results showed that MOX treatments had a much stronger impact on Pinot noir wines with higher phenolic content including more monomeric anthocyanins (i.e., PN2), which can be combined to form coloured polymeric pigments.

After the final SO_2 addition, measured at day 48, the absorbance at 420 nm and 520 nm and colour intensity decreased in all treatments. However, a greater decline appeared in wines with MOX (8~26 %) compared to the control wines (5~15 %) and especially for T3 and T4. This could be due to the bleaching of anthocyanins derived from self-association and co-pigmentation reactions (Boulton, 2001) that were previously promoted by MOX. As a result, in both PN1 and PN2, no significant variation was found between the control and MOX treatments in the 420 nm and 520 nm absorbances and colour intensity in the end. Nevertheless, the content of SO_2 resistant pigments remained significantly higher in T2, T3 and T4, therefore, MOX still had a durable influence on the evolution of coloured pigments in these wines. In PN2, a further decrease in the monomeric (except for T4) and total anthocyanins (up to 7 % and 8 %, respectively) was also observed and the final concentrations were significantly lower in T3 and T4. However, these were not found in T1 and T2.

For the polymeric pigments measured using the Harbertson-Adams assay, SPP are a heterogeneous mixture of anthocyanin derived products that do not precipitated with protein and LPP from anthocyanins reacting with tannins that do (Harbertson *et al.,* 2003). In PN1 wines, SPP decreased across all treatments (Figure 3c), while a higher increase of LPP (Figure 3d) was found in T1 and T2 ($p < 0.05$), showing the interactions

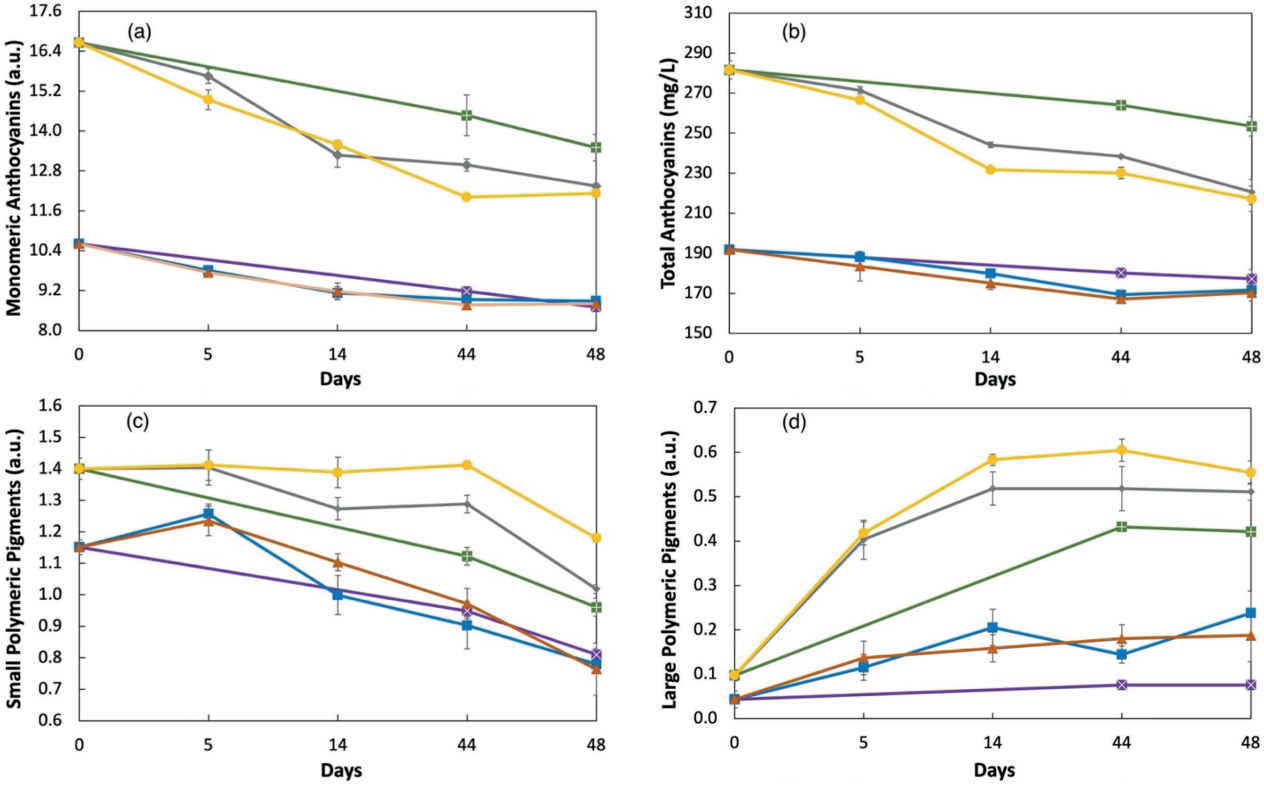

FIGURE 3. Effect of MOX at 0.50 and 2.11 mg/L/day for 14 days on Pinot noir wines with a low phenolic content (T1 and T2) and a high phenolic content (T3 and T4) compared to the controls (C1 and C2, respectively) on the change of colour absorbance by spectrophotometric measures for (a) monomeric anthocyanins, by the Harbertson-Adams assay for (b) total anthocyanins (mg/L, malvidin-3-glucosie equivalents), (c) small polymeric pigments, and (d) large polymeric pigments (mean ± standard error, n = 6).

TABLE 3. Influence of MOX on Pinot noir wines with a low phenolic content (T1 and T2) and a high phenolic content (T3 and T4) compared to the controls (C1 and C2, respectively) on the composition of monomeric phenolics (mean ± standard error, n = 6).

Timeline &Treatments	Parameters						
	Gallic acid	Catechin	Vanillic acid	Syringic acid	Epicatechin	Trans-caftaric acid	Cis-coutaric acid
LOD (mg/L)	0.1	0.6	0.3	0.3	0.8	0.1	0.2
LOQ (mg/L)	0.2	1.8	1.1	0.8	2.8	0.4	0.6
Pinot noir 1 (C1, T1 and T2)							
Time 0	37.4 ± 0.1	190.5 ± 2.1	4.2 ± 0.4	5.4 ± 0.1	91.9 ± 2.3	24.8 ± 0.3	2.7 ± 0.1
Day 44 (after ageing for 1 month)							
C1 (Control no MOX)	38.1 ± 0.2 a	196.8 ± 1.4 a	3.6 ± 0.4 a	5.4 ± 0.4 a	90.0 ± 3.4 a	25.8 ± 0.1 a	2.3 ± 0.0 a
T1 (Low MOX dose)	38.0 ± 0.3 a	177.1 ± 4.0 b	3.5 ± 0.3 a	5.5 ± 0.5 a	90.2 ± 2.3 a	25.7 ± 0.2 a	2.3 ± 0.0 a
T2 (High MOX dose)	38.3 ± 0.3 a	169.1 ± 5.9 b	3.0 ± 0.2 a	5.6 ± 0.4 a	87.6 ± 4.1 a	26.0 ± 0.0 a	2.3 ± 0.0 a
Day 48 (after SO_2 addition)							
C1 (Control no MOX)	38.2 ± 0.2 a	192.5 ± 6.7 a	3.3 ± 0.3 a	4.4 ± 0.1 a	88.8 ± 0.5 a	25.7 ± 0.0 a	2.3 ± 0.0 a
T1 (Low MOX dose)	38.3 ± 0.4 a	173.3 ± 5.3 b	3.9 ± 0.4 a	4.7 ± 0.4 a	87.3 ± 1.1 a	25.7 ± 0.2 a	2.3 ± 0.0 a
T2 (High MOX dose)	37.9 ± 0.1 a	163.8 ± 1.4 b	3.9 ± 0.2 a	5.0 ± 0.2 a	82.9 ± 1.6 a	25.9 ± 0.0 a	2.4 ± 0.0 a
Pinot noir 2 (C2, T3 and T4)							
Time 0	44.8 ± 0.6	241.9 ± 1.6	8.6 ± 0.5	15.7 ± 0.1	147.3 ± 5.5	34.0 ± 0.1	3.5 ± 0.1
Day 44 (after ageing for 1 month)							
C2 (Control no MOX)	43.7 ± 1.1 a	235.3 ± 2.5 a	5.5 ± 0.7 a	15.8 ± 0.3 a	139.0 ± 1.8 a	34.6 ± 0.1 a	3.3 ± 0.1 a
T3 (Low MOX dose)	44.0 ± 0.6 a	232.4 ± 2.2 a	4.9 ± 0.6 a	15.4 ± 0.3 a	126.7 ± 4.0 b	29.8 ± 7.5 a	3.4 ± 0.1 a
T4 (High MOX dose)	44.0 ± 0.5 a	222.8 ± 1.6 b	5.4 ± 0.4 a	15.0 ± 0.4 a	122.1 ± 2.8 b	33.7 ± 0.1 a	3.2 ± 0.1 a
Day 48 (after SO_2 addition)							
C2 (Control no MOX)	45.2 ± 0.2 a	236.1 ± 3.2 a	5.2 ± 1.1 a	15.3 ± 0.1 a	138.5 ± 0.1 a	34.8 ± 0.4 a	3.6 ± 0.3 a
T3 (Low MOX dose)	45.7 ± 0.1 a	230.8 ± 1.2 a	4.5 ± 0.4 a	15.0 ± 0.1 a	126.0 ± 0.2 b	34.5 ± 0.3 a	3.5 ± 0.2 a
T4 (High MOX dose)	46.0 ± 0.1 a	221.6 ± 1.6 b	4.8 ± 1.0 a	15.1 ± 0.2 a	124.8 ± 1.6 b	34.3 ± 0.3 a	3.4 ± 0.1 a

Values are presented as mean ± standard error (n = 6); different letters in a column are significantly different (Tukey $p < 0.05$). m-3-g: malvidin-3-glucoside, ND, not detected; BLOQ, below the quantification limit.

Timeline &Treatments	Parameters						
	Trans-coutaric acid	Caffeic acid	Coumaric acid	Quercetin glucuronide	Quercetin glucoside	Quercetin	Malvidin-3-glucoside
LOD (mg/L)	0.2	0.1	0.2	1.0	1.0	1.0	1.3
LOQ (mg/L)	0.6	0.4	0.6	3.3	3.3	3.3	4.5
Pinot noir 1 (C1, T1 and T2)							
Time 0	3.6 ± 0.1	7.8 ± 0.0	2.3 ± 0.0	17.4 ± 0.3	0.9 ± 0.1	33.3 ± 0.2	92.3 ± 0.4
Day 44 (after ageing for 1 month)							
C1 (Control no MOX)	3.4 ± 0.1 a	7.9 ± 0.1 a	2.5 ± 0.0 a	18.9 ± 0.1 a	ND	31.7 ± 0.7 a	81.5 ± 0.2 a
T1 (Low MOX dose)	3.3 ± 0.1 a	7.9 ± 0.1 a	2.5 ± 0.0 a	18.7 ± 0.1 a	ND	25.0 ± 0.2 b	77.8 ± 1.3 b
T2 (High MOX dose)	3.4 ± 0.1 a	8.0 ± 0.1 a	2.5 ± 0.0 a	19.0 ± 0.2 a	ND	22.0 ± 0.9 b	77.0 ± 1.5 b
Day 48 (after SO_2 addition)							
C1 (Control no MOX)	3.3 ± 0.0 a	8.0 ± 0.0 a	2.5 ± 0.0 a	19.1 ± 0.0 a	ND	32.6 ± 0.6 a	72.4 ± 0.8 a
T1 (Low MOX dose)	3.3 ± 0.0 a	7.9 ± 0.1 a	2.5 ± 0.0 a	19.3 ± 0.6 a	ND	26.7 ± 0.4 b	68.7 ± 1.0 a
T2 (High MOX dose)	3.4 ± 0.0 a	7.8 ± 0.0 a	2.6 ± 0.0 a	19.0 ± 0.1 a	ND	23.5 ± 0.5 c	68.8 ± 0.7 a
Pinot noir 2 (C2, T3 and T4)							
Time 0	4.5 ± 0.0	12.0 ± 0.0	4.7 ± 0.0	21.9 ± 0.1	5.9 ± 0.1	48.0 ± 0.4	144.5 ± 1.1
Day 44 (after ageing for 1 month)							
C2 (Control no MOX)	4.2 ± 0.1 a	10.4 ± 0.3 a	5.6 ± 0.1 a	22.3 ± 0.1 a	BLOQ	45.5 ± 0.4 a	121.4 ± 1.6 a
T3 (Low MOX dose)	4.1 ± 0.1 a	10.6 ± 0.2 a	5.5 ± 0.1 a	21.1 ± 0.4 a	BLOQ	39.3 ± 0.6 b	84.6 ± 2.8 b
T4 (High MOX dose)	4.1 ± 0.1 a	10.7 ± 0.3 a	5.5 ± 0.1 a	21.6 ± 0.5 a	BLOQ	32.2 ± 1.2 c	75.7 ± 0.5 c
Day 48 (after SO_2 addition)							
C2 (Control no MOX)	4.0 ± 0.1 a	10.5 ± 0.0 a	5.5 ± 0.0 a	22.5 ± 0.0 a	BLOQ	45.8 ± 0.6 a	108.9 ± 0.9 a
T3 (Low MOX dose)	4.0 ± 0.2 a	10.8 ± 0.2 a	5.5 ± 0.0 a	21.6 ± 0.0 b	BLOQ	38.9 ± 0.7 b	75.5 ± 1.3 b
T4 (High MOX dose)	3.9 ± 0.1 a	10.5 ± 0.1 a	5.5 ± 0.0 a	21.1 ± 0.2 b	BLOQ	32.9 ± 1.1 c	68.7 ± 1.0 c

Values are presented as mean ± standard error (n = 6); different letters in a column are significantly different (Tukey $p < 0.05$). m-3-g: malvidin-3-glucoside, ND, not detected; BLOQ, below the quantification limit.

between tannins and anthocyanins in the presence of oxygen (He *et al.,* 2012) in these wines. At wine pH, this has been shown to generate coloured flavyliums, which would explain the increase in the 420 nm and 520 nm absorbances and colour intensity in T1 and T2. In PN2 wines, on the contrary, SPP remained almost unchanged in T4 and only slightly decreased in T3 after MOX, compared to a higher decline in C1. Meanwhile, LPP increased in PN2 wines over time, including the control (C2), but were significantly higher in T3 and T4. Therefore, to wines with the higher initial phenolic content, MOX had not only significantly promoted anthocyanin condensation reactions with tannins, but also maintained a higher concentration of polymeric pigments with anthocyanin colour. These variations between PN1 and PN2 reflected their differences in the anthocyanin content.

After SO_2 addition, a decline of SPP was seen in all wines (i.e., 15 % in C1, 13 % in T1, and 22 % in T2; 14 % in C2, 21 % in T3 and 16 % in T4), while the LPP content in wines remained similar to these before the SO_2 addition. The latter can be linked to the content of SO_2 resistant pigments in these wines. The decline in SPP would have contributed to the loss of wine colour at 420 nm and 520 nm absorbances and colour intensity observed after SO_2 addition. Cheynier *et al.* (2006) reported that the stability of pigments is not related to molecular weight, as some polymeric pigments are exactly like the anthocyanin precursors and are not resistant to sulfite bleaching. Moreover, the limited acetaldehyde production could lead to a lower content of acetaldehyde-mediated pigments in the wines. The importance of acetaldehyde on increasing colour stability and intensity has been well discussed, promoting pigment formation with the ethyl-bridged covalent bond that is more resistant to cleavage and SO_2 bleaching (Escribano-Bailón *et al.,* 2001; Picariello *et al.,* 2017; Han *et al.,* 2019). In a recent study (Yang *et al.,* 2021a), after SO_2 addition, a decrease of 520 nm absorbance and colour intensity was also observed in wines with MOX applied after MLF (approximately 6 % and 4 %, respectively), which, however, were much less than in the control treatments (approximately 15 % and 12.5 %, respectively). The acetaldehyde production in this previous study (Yang *et al.,* 2021a) was at least 10 times higher than in the present study. Nevertheless, the content of SO_2 resistant pigments remained significantly higher in T2, T3 and T4. Therefore, MOX still had a durable influence on coloured pigments evolution. The trends seen in the present study could also suggest further modifications on the small polymeric anthocyanins, as well as reactions with other phenolic compounds released from SO_2 cleavage reactions to form colourless species, e.g., some of the anthocyanin-tannin adducts (Remy and Moutounet, 2000). Together, these could have also contributed to the decrease in wine colour observed in all wines after SO_2 addition.

3. Monomeric phenolic content

A total of 14 monomeric phenolics, including hydroxycinnamic and hydroxybenzoic acids, flavan-3-ols, flavonols and malvidin-3-glucoside, were identified in the two Pinot noir wines at the beginning of the experiment (except for ferulic acid in PN1) (Table 3). Their initial concentrations were higher in PN2, indicating a higher co-pigmentation capacity (Boulton, 2001). The monomeric phenolics were analysed again at day 44 and after the final SO_2 addition at day 48. With MOX treatments, significant declines were found in the concentration of malvidin-3-glucoside (i.e., the only monomeric anthocyanin detected), flavan-3-ols, and several flavonols.

In both PN1 and PN2, the decline in malvidin-3-glucoside was consistent with the results of spectrophotometric measures of monomeric and total anthocyanins. Between the control wines, the decrease in C2 was close to 2 times higher than in C1. Under the same MOX dosage, the overall decrease in PN1 was minimal (i.e., up to about 5 mg/L) compared to in PN2 (i.e., around 30 to 50 mg/L). After SO_2 addition, a further decrease of malvidin-3-glucoside was found, although this was not large (i.e., up to 12 mg/L). For the flavan-3-ols, the decrease in (+)-catechin induced by MOX was much greater in PN1, which was approximately 2 times more in T2 than T4 and only occurred in PN1 at the lower MOX dosage (T1). Meanwhile, a decrease in (-)-epicatechin by MOX was only found in PN2.

Among the flavonols, quercetin, and quercetin-3-glucoside, decreased during the experiment. Quercetin in the free form is an important cofactor for anthocyanin co-pigmentation (Boulton, 2001; He *et al.,* 2012) and is also prone to oxidation (Zenkevich *et al.,* 2007). In the control treatments, the decrease of quercetin from time 0 to the endpoint was very small, by less than 1 mg/L in C1 and around 2 mg/L in C2. With MOX, a higher decrease in quercetin was found in both PN1 and PN2. Under the same oxygen dosage, the decrease of quercetin in wines at the endpoint

TABLE 4. Influence of MOX on Pinot noir wines with a low phenolic content (T1 and T2) and a high phenolic content (T3 and T4) compared to the controls (C1 and C2, respectively) on the tannin composition (mean ± standard error, n = 6).

Timeline & Treatments	Parameters											
	MCP Tannin (g/L)	Tannin Yield %	mDP	Extension Unit (mole) %				Terminal Unit (mole) %			%Tri-OH	%Gall
				EGC	CAT	EPI	ECG	CAT	EPI	ECG		
Pinot noir 1 (C1, T1 and T2)												
Time 0	0.45 ± 0.01	68 ± 2	2.2 ± 0.0	9.0 ± 0.1	7.7 ± 0.0	44.8 ± 0.0	1.9 ± 0.0	13.8 ± 0.1	14.8 ± 0.0	8.1 ± 0.0	9.0 ± 0.1	10.0 ± 0.0
Day 44 (after ageing for 1 month)												
C1 (Control no MOX)	0.62 ± 0.02 b	60 ± 1 a	2.2 ± 0.0 a	8.7 ± 0.2 a	6.8 ± 0.1 a	44.4 ± 0.3 a	2.2 ± 0.0 a	13.0 ± 0.1 b	17.3 ± 0.3 b	7.7 ± 0.3 b	8.7 ± 0.2 a	10.0 ± 0.2 b
T1 (Low MOX dose)	0.64 ± 0.01 b	57 ± 1 a	2.1 ± 0.0 a	7.8 ± 0.2 a	6.9 ± 0.1 a	43.7 ± 1.1 a	2.2 ± 0.0 a	13.9 ± 0.5 ab	17.5 ± 0.2 b	8.0 ± 0.1 b	7.8 ± 0.2 a	10.2 ± 0.1 b
T2 (High MOX dose)	0.82 ± 0.03 a	48 ± 0 b	1.9 ± 0.0 b	6.8 ± 0.1 b	6.1 ± 0.1 b	41.3 ± 0.5 b	2.4 ± 0.0 a	15.3 ± 0.0 a	19.1 ± 0.2 a	8.9 ± 0.1 a	6.8 ± 0.1 b	11.3 ± 0.1 a
Day 48 (after SO_2 addition)												
C1 (Control no MOX)	0.66 ± 0.04 a	55 ± 0 a	2.2 ± 0.0 a	8.8 ± 0.1 a	8.6 ± 0.1 a	43.0 ± 0.6 a	1.6 ± 0.0 a	15.2 ± 0.1 a	15.4 ± 0.1 b	7.2 ± 0.2 a	8.8 ± 0.1 a	8.9 ± 0.2 a
T1 (Low MOX dose)	0.64 ± 0.03 a	50 ± 1 b	2.1 ± 0.0 a	7.1 ± 0.1 b	8.6 ± 0.5 a	43.6 ± 0.7 a	1.7 ± 0.0 a	15.7 ± 0.2 a	15.7 ± 0.2 ab	7.6 ± 0.1 a	7.1 ± 0.1 b	9.3 ± 0.1 a
T2 (High MOX dose)	0.78 ± 0.01 b	43 ± 1 c	2.1 ± 0.0 a	7.1 ± 0.4 b	6.8 ± 0.2 b	43.8 ± 0.2 a	1.8 ± 0.0 a	16.5 ± 0.2 a	16.4 ± 0.2 a	7.5 ± 0.1 a	7.1 ± 0.4 b	9.3 ± 0.1 a
Pinot noir 2 (C2, T3 and T4)												
Time 0	0.67 ± 0.01	60 ± 2	2.4 ± 0.0	9.9 ± 0.1	7.4 ± 0.0	47.2 ± 0.4	1.8 ± 0.0	12.8 ± 0.2	13.7 ± 0.1	7.1 ± 0.1	9.9 ± 0.1	8.9 ± 0.1
Day 44 (after ageing for 1 month)												
C2 (Control no MOX)	0.88 ± 0.01 b	58 ± 1 a	2.3 ± 0.0 a	6.7 ± 0.6 a	7.5 ± 0.2 a	48.4 ± 0.7 a	1.3 ± 0.0 a	12.8 ± 0.2 a	16.6 ± 0.4 a	6.7 ± 0.0 a	6.7 ± 0.6 a	8.0 ± 0.0 a
T3 (Low MOX dose)	0.97 ± 0.01 a	54 ± 1 ab	2.3 ± 0.0 a	4.7 ± 0.2 b	7.2 ± 0.1 a	50.2 ± 0.2 a	1.4 ± 0.0 a	12.8 ± 0.5 a	17.4 ± 0.3 a	6.4 ± 0.1 a	4.7 ± 0.2 b	7.7 ± 0.2 a
T4 (High MOX dose)	0.95 ± 0.01 a	53 ± 1 b	2.2 ± 0.0 a	5.3 ± 0.2 b	7.1 ± 0.2 a	49.2 ± 0.4 a	1.5 ± 0.1 a	13.0 ± 0.3 a	17.5 ± 0.2 a	6.4 ± 0.1 a	5.3 ± 0.2 b	7.9 ± 0.2 a
Day 48 (after SO_2 addition)												
C2 (Control no MOX)	0.84 ± 0.04 b	59 ± 3 a	2.3 ± 0.0 a	6.5 ± 0.2 a	7.1 ± 0.0 a	48.9 ± 0.6 a	1.6 ± 0.0 a	12.1 ± 0.1 a	17.1 ± 0.1 a	6.7 ± 0.0 a	6.5 ± 0.2 a	8.3 ± 0.1 a
T3 (Low MOX dose)	0.92 ± 0.01 ab	54 ± 1 a	2.2 ± 0.0 a	4.6 ± 0.1 b	6.9 ± 0.1 a	49.7 ± 0.5 a	1.7 ± 0.0 a	13.3 ± 0.8 a	17.3 ± 0.2 a	6.5 ± 0.3 a	4.6 ± 0.1 b	8.2 ± 0.3 a
T4 (High MOX dose)	0.98 ± 0.03 a	53 ± 2 a	2.2 ± 0.0 a	4.5 ± 0.1 b	6.8 ± 0.0 a	49.5 ± 0.0 a	1.6 ± 0.2 a	13.5 ± 0.4 a	17.7 ± 0.1 a	6.5 ± 0.1 a	4.5 ± 0.1 b	8.1 ± 0.3 a

Values are presented as mean ± standard error (n = 6); different letters in a column are significantly different (Tukey $p < 0.05$). MCP Tannin: tannin concentration ((-)-epicatechin equivalent, g/L) determined by methylcellulose assay; Tannin Yield%: depolymerisable tannins; mDP: mean degree of polymerisation; EGC: (-)-epigallocatechin; CAT: (+)-catechin; EPI: (-)-epicatechin; ECG: (-)-epicatechin gallate; %Tri-OH: percentage of tri-hydroxylation, (-)-epigallocatechin extension unit; %Gall: percentage of galloylation, sum of (-)-epicatechin gallate extension and terminal units.

was somewhat similar, which was around 20 % and 19 % in T1 and T3, respectively, and higher at 29 % and 31 % with the higher oxygen dosage in T2 and T4, respectively. Thus, the influence of MOX on quercetin appeared to be dependent on the oxygen dosage and also in proportion to its initial content. Finally, similar losses of quercetin-3-glucoside were observed in PN2 with time, independent of the treatments, suggesting a loss due to the hydrolysis mechanism that was not affected by MOX. In PN1, quercetin-3-glucoside was not detected in the end.

4. Tannin composition

Results for the tannin profiles of the wines are presented in Table 4. The tannin concentration (i.e., tannin reactive with methylcellulose) increased in all wines during this experiment, but with a greater percentage increase in PN1 (30 % to 42 %) than in PN2 (22 % to 32 %). SO_2 addition did not show a clear impact on tannin concentration. In the end, the highest tannin concentration in both PN1 and PN2 was found with the highest oxygen dosage (T2 and T4). Oxidised tannins found in the modality are known to have greater intramolecular interactions, forming more condensed structures. However, this might have a negative impact on perceived astringency, which has been shown to increase with a higher tannin concentration (McRae and Kennedy, 2011). Despite the increase in tannin concentration, the mDP of tannins in both PN1 and PN2 remained very small (~2) and was not affected by MOX or the initial polyphenol content. This might be associated with the varietal characteristics of Pinot noir grapes that have a lower skin to seed tannin ratio (Sparrow *et al.,* 2016), in which skin tannins are known to have a higher mDP (3 to 83), while a lower mDP (2 to 17) has been associated with seed tannins (McRae and Kennedy, 2011; Harrison, 2018). It needs to be also recognised that the measured mDP only applies to depolymerisable tannins, namely the molecules that can be broken up in the phloroglucinolysis reaction, which in the studied wines was no more than 60 % towards the end of the trial.

The yield (%) of total tannin polymers from the phloroglucinolysis reaction decreased in all wines, particularly with the T2 treatment of PN1. Together with the higher increase in tannin concentration, this showed a stronger impact of the higher MOX dosage on PN1, seen here by there being more tannin macromolecules that could not be easily depolymerised. Additionally, a loss in tannin yield (%) can also be associated with the formation of pyranoanthocyanins (McRae *et al.,* 2015). The authors reported a lower tannin yield (%) when more pigmented tannins were present, due to a decline in the acid-labile bonds in the newly formed pigmented tannins. In theory, this would have affected PN2 with MOX more than PN1, due to the much larger increase in polymeric pigments. However, this was not the case in the present study. Here, the influence of pigment types on tannin composition and yield (%) determined by the phloroglucinolysis reaction needs to be considered, as Pinot noir wines are lacking in acetylated anthocyanins. This will require further investigation.

After SO_2 addition, a further decrease in tannin yield (5~7 %) was found in PN1, but not in PN2. It is well known that wine tannins can react with SO_2, forming sulfonated flavanols at the terminal positions (Ma *et al.,* 2018). This group of tannin molecules are unfortunately not measured by the phloroglucinolysis method. Currently, tannin sulfonation has only been reported in wines after a long period of ageing (Ma *et al.,* 2018, Arapitsas *et al.,* 2018; Watrelot *et al.,* 2020), while in model wine solutions they have been detected soon after SO_2 addition (Bonaldo *et al.,* 2020). Future studies will be required to investigate the impact of tannin sulfonation on young red wines. Another possibility is that SO_2 addition may have resulted in bond breaking with some of the tannins producing smaller molecules (Ma *et al.,* 2018), which could then undergo rearrangement reactions and even tannin polymerisation (McRae and Kennedy, 2011). For the PN2 wines, the influence of SO_2 on tannin composition may have been lower due to coloured polyphenols reacting with SO_2 in preference to the tannins, as seen by the larger decline in colour parameters with the PN2 wines described above. The variation in tannin yield (%) loss in response to SO_2 addition can therefore be associated with the differences in phenolic content between PN1 and PN2.

Regarding tannin composition, the degree of galloylation (%Galloyl) remained similar across all treatments, whereas trihydroxylation (%Tri-OH, (-)-epigallocatechin extension units) significantly declined in both PN1 and PN2 with MOX. In Yang *et al.* (2021b), an increase of %Galloyl was found in Pinot noir wines following MOX, although the wines had commercial tannin and oak products added at primary fermentation. The hydrolysis of gallate esters is known to occur during wine ageing but is not always directly affected by oxidation (Watrelot *et al.,* 2020).

In the present study, commercial tannin and oak products were not used, and the role of such additives on the evolution of Pinot noir tannin composition during MOX deserves further investigation.

A decrease in (-)-epigallocatechin extension units, associated with skin-derived tannins, was observed in both Pinot noir wines. Such a decrease in response to oxygen exposure has been reported previously in model wines (Lee, 2010; Carrascón *et al.,* 2018), and in wines subject to oxygenation (McRae *et al.,* 2015; Watrelot *et al.,* 2020; Yang *et al.,* 2021b), with linkage made to the impact of *Saccharomyces cerevisiae* as having a high affinity towards (-)-epigallocatechin units (Mazauric and Salmon, 2005). In Watrelot *et al.* (2020), this influence of oxygen on (-)-epigallocatechin extension unit was recorded in wines even after ageing for 3 years. This trends, seen here in the absence of yeast effects, could be an unwanted outcome, as (−)-epigallocatechin has been suggested as being responsible for the softer taste in skin tannins despite higher mDP values (Fernández *et al.,* 2007; Ma *et al.,* 2014), and for decreasing the perception of "coarse" sensations from tannins (Vidal *et al.,* 2003). Also, (-)-epigallocatechin has been shown to have a weaker cellular response to human bitter taste receptors than the galloyl group of tannin subunits (Narukawa *et al.,* 2011).

Besides the loss of (-)-epigallocatechin extension units, no other significant variation was found in PN2 wines between the treatments. In PN1 wines, before SO_2 addition, a decrease of (+)-catechin and (-)-epicatechin extension units was observed in T2, which led to a higher proportion of (+)-catechin, (-)-epicatechin and (-)-epicatechin-gallate terminal units in the depolymerised tannins. Tannin self-association and condensation reactions could have played a role in the changes seen in tannin composition seen with the phloroglucinolysis procedure. The final SO_2 addition affected the tannin subunits in PN1, where a decrease in the (-)-epicatechin terminal units and increase in (+)-catechin terminal units was observed. This is also of concern, as a larger proportion of catechin subunits could also enhance tannin binding with salivary proteins (McRae and Kennedy, 2011).

CONCLUSIONS

MOX treatments showed significant but varied impacts on the two Pinot noir wines, which had different initial phenolic contents. In PN2, with the higher phenolic content, MOX induced a much greater increase in the 420 nm and 520 nm absorbances, colour intensity and SO_2 resistant pigments, in association with a higher increase in SPP and LPP content. At the same time, the increase of acetaldehyde by MOX in the present study was much lower than in previous studies in which significant yeast activity was also seen to occur.

With MOX, a greater decline in (+)-catechin was observed in the PN1 wines, contributing to the changes in tannin composition. Meanwhile, (-)-epicatechin significantly decreased only in the PN2 wines. A decline of quercetin was found with MOX, and more so with a higher oxygen dosage rate. A greater impact on the tannin composition was observed with PN1, especially with the higher oxygen dosage, leading to a large decrease in the tannin yield (%) and (+)-catechin extension units, while increasing the proportion of terminal units. MOX also accelerated the decrease in skin tannin derived (-)-epigallocatechin extension units in both PN1 and PN2 and increased tannin concentration (except for T1). These changes in phenolic composition might lead to an increase of perceived astringency, which could be a drawback for MOX on Pinot noir wines, especially lower phenolic content wines such as PN1. The results also showed that the same winemaking treatment could have varied impacts on Pinot noir wines with different phenolic contents.

The final SO_2 addition (100 mg/L) had a substantial impact on the wines, cancelling out the improvement of colour provided by MOX for the PN2 wines (except for the SO_2 resistant pigments) and further lowering the tannin yield (%) in the PN1 wines. The loss of colour could be due to the bleaching of self-associated and co-pigmented anthocyanins, which with limited acetaldehyde available in these wines (only up to 11.5 mg/L), produced fewer acetaldehyde-mediated stable pigments, which should be investigated further along with research into tannin sulfonation in Pinot noir wines.

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