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Univ. Bordeaux, ISVV, EA 4577, Œnologie, 210 Chemin de Leysotte, 33140 Villenave d'Ornon, France

INRA, ISVV, USC 1366 Œnologie, 210 Chemin de Leysotte, 33140 Villenave d'Ornon, France

* e-mail: kleopatra.chira@u-bordeaux.fr

Abstract

Haloanisoles (HAs) are known to compromise wine quality because of their mouldy off-flavours. Up to now no treatment exists to eliminate the presence of these unpleasant volatiles in wine. This research aimed i) to assess the alimentary plastic film efficacy to remove or lessen HAs content in polluted wines; and ii) to evaluate its impact on wine quality. The film-treatment reduced significantly (p<0.05) the 2,4,6-trichloroanisole (TCA) content of initial wine. This decrease became more noticeable as the contact time film-wine increased.

Chromatic characteristics, phenolic and proanthocyanidin contents, and woody aroma profile did not change because of the film treatment. A significant sorption of certain esters was observed, but as HAs were removed under detection thresholds, fruity perception of wines was improved.

Globally, the alimentary plastic film was able to improve the organoleptic quality of wines contaminated with HAs, by reducing the cork taint and enhancing their overall fruity aroma.

Keywords 2,4,6-trichloroanisole, oak wood barrel, plastic film, phenolic composition, aroma profile, sensory analysis

1. Introduction

The mouldy, musty, earthy or 'wet cardboard' off-flavours in wine commonly called « cork taint » are a serious quality-related problem for wine industry. There is no official information about the real incidence and the whole economic losses incurred worldwide by cork-tainted wine (Garde-Cerdán, Lorenzo, Zalacain, Alonso, & Salinas, 2012), but at least 5% of the bottled wines are affected (Sefton & Simpson, 2005).

At the beginning of the eighties, the 2,4,6-trichloroanisole (TCA) was identified as the main component responsible for this flavour-damaging effect in wines (Buser, Zanier, & Tanner, 1982). Although different compounds (geosmin, 1-octen-1-ol, 1-octen-3-one, 2-methylisoborneol, pyrazines, among others) have been claimed to be involved in this wine defect (Callejon, Ubeda, Rios-Reina, Morales, & Troncoso, 2016), research has been mainly focused on haloanisoles (HAs) and their corresponding precursors, halophenols (HPs). This choice is especially driven by the low detection threshold values of HAs (part-per-trillion range, ng/L), making possible their detection by consumers even under trace amounts. The occurrence of these volatile compounds in wine notably decrease its organoleptic quality, by masking the fruity notes (Tempere, Schaaper, Cuzange, de Revel, & Sicard, 2017), and compromise the consumer acceptance of the product (Prescott, Norris, Kunst, & Kim, 2005).

Until fairly recently, this off-flavour was erroneously considered as cork-derived, but nowadays it is well known that corks are just one of many other possible sources of contamination. HAs are very volatile and become airborne, thus, they may be transferred into wine through the cellar's atmosphere or by contact or storage with contaminated material (water, oak products, plastics...). Scientific data have shown that the actual origin of wine spoilage by these organohalogen compounds is in fact a problem of environmental contamination (Copete et al., 2009). According to the literature, HAs result from biomethylation of HPs by different microorganisms (fungi, molds and/or bacteria, still not identified), under particular conditions of temperature and humidity (Riu, Mestres, Busto, & Guasch, 2006). During the twentieth century, these HPs have been widely used as

biocides (herbicides, insecticides and fungicides) in agriculture, and as wood preservatives and flame-retardants in industry, contributing to their air, water and soil accumulation. Furthermore, consistent data reveal their potential formation in the environment by low levels of anthropogenic chlorine (urban water supply, sanitizer and/or cleaning products) and endogenous phenols from plant material (Simpson & Sefton, 2007).

Chatonnet *et al.* (2010) revealed TCA contamination of wines that have had no contact with polluted corks, but acquired mouldy character from oak wood of new barrels used to age wine. The authors highlighted that both coopers and barrel-users seriously underestimate the problem, because the localized and random pollution of barrel staves by HAs and/or HPs makes difficult their systematic detection. According to the French Coopers Federation, the suspect cases only represent around 0.04% of barrel production and there is no significant accentuation in recent years. Meanwhile, to ensure a complete traceability to their customers, coopers increasingly control the presence of these undesirable compounds.

From forest to shipping, different potential entry points of both HAs and HPs may be considered for oak wood pollution during barrel manufacture. Since the origin of HAs and HPs contamination for oak wood is not clearly identified at each individual cooperage, different strategies (yeast hulls, Fibrafix TX-R filter sheets, plastic film, milk products, grape seeds oil) are searched to eliminate or lessen the presence of these unpleasant volatile compounds in wine (Jung, Schaefer, Christmann, Hey, Fischer, & Rauhut, 2008; Mirabel, de Beauregard, Riquier, & Bertrand, 2006; Vidal, Puech, Fernández, Fauveau, Pellerin, & Vuchot, 2007). Some taste and/or aroma distorting and/or reduction effects have been noted for some of these treatments. Unfortunately, a lack of in-depth information about their impact on wine matrix and quality seems to limit significantly their widespread use in wine industry.

Within this context, the present research aimed i) to assess the efficacy of a plastic film (certified for alimentary uses) to remove or lessen the HAs and HPs content in polluted wines; and ii) to evaluate its impact on wine quality and more particularly on the

83 oenological and chromatic parameters, phenolic composition, analytical profile of aroma
84 compounds and sensory attributes of those wines.

2. Materials and methods

2.1 Oak wood origin and drying conditions

All barrels used were made up of French oak from two species (*Quercus robur* and *Quercus petraea*) from the same forest located in the Center region of France. The raw staves (100 cm x 11 cm x 0.12 cm) were naturally seasoned for 24 months in a wood yard. Once assembled, barrels (225 L) were submitted to a medium toast (68 min at 57±3 ºC) using the traditional way over an oak wood fire. The barrel heads were not toasted. For the purpose of the study, three barrels (A, B, C) with a different level of HAs and HPs pollution were provided to the wine cellar. From barrel A to C, an increasing level of HAs and HPs pollution was confirmed.

2.2 Red wine vinification

Cabernet Sauvignon (70%) and *Merlot* (30%) grapes (*Vitis vinifera* L.) were manually harvested at maturity during the 2013 vintage. The same day, grapes were crushed and destemmed. Potassium metabisulphite (5.0 ± 0.5 g/hL) was added during the transfer of must to stainless steel tanks and *Saccharomyces cerevisiae* was included to perform alcoholic fermentation at 25-30 ºC. Then, malolactic fermentation extended for one month at a maintained temperature of 20 ºC and its development was controlled by monitoring the L-malic acid content of the wines.

Once the MLF was finished (malic acid content ≤ 0.4 g/L), wines were racked, additionally sulfitated (3.0 – 3.5 g/hL) and transferred to oak barrels for ageing during 24 months at a controlled temperature of 15-16 ºC.

2.3 Wine treatment and sample collection

At the end of the 24-months ageing, wine was transferred to stainless steel tanks to perform the film-treatment. A plastic film, composed of a mixture of synthetic polymers and certified for alimentary uses (no migration of plastic molecules to wine takes place) was added to the wine at a dose of 20 m^2 film/hL.

111 Wine was sampled after 8, 24 and 48h of wine-film contact, and then, bottled and stored at
112 16 ºC until further analysis. All bottle caps were covered with aluminum foil to avoid a
113 sorption or a second potential entry of compounds contributor to cork taint.

114 **2.4 Oenological and chromatic parameters in wines**

115 Conventional oenological parameters of wines, i.e., pH, density (g/L), alcoholic degree (%),
116 both titratable and volatile acidity (g tartaric acid/L), glucose/fructose ratio (GFR), total
117 polyphenol index (TPI) and malic, lactic and tartaric acid contents (g/L), were determined
118 in duplicate by Infrared Spectrometry with Fourier Transformation (IRTF) with a
119 WineScan^{TM} Flex (FOSS Analytical, Denmark), which was previously calibrated with wine
120 samples analyzed in accordance with official OIV methods (OIV, 2016).
121 Chromatic parameters of wines, i.e., absorbance's at 420 (d420), 520 (d520) and 620 nm
122 (d620) were also measured in triplicate under 1 mm optical way with a V-630 UV-VIS
123 spectrophotometer (JASCO, Japan). The color intensity (CI, sum of the three absorbances),
124 the hue (d420/d520) and the components yellow (d420%), red (d520%) and blue (d620%)
125 were calculated.

126 **2.5 Total phenolics, proanthocyanidins and anthocyanins analyses**

127 A modified Folin Ciocalteu method to be applied in 96-well microplates (González-
128 Centeno, Chira, & Teissedre, 2016) was used to measure total phenolics with an automated
129 microplate reader (FLUOstar Optima, BMG LabTech, France). Proanthocyanidin and
130 anthocyanin contents of wines were also spectrophotometrically determined, by using the
131 same UV-Vis equipment as for chromatic parameters, through the Bate-Smith reaction
132 (Ribereau-Gayon & Stonestreet, 1966) and the sodium bisulfite discoloration method
133 (Ribereau-Gayon & Stonestreet, 1965), respectively. Wines were diluted in water at a ratio
134 1:20 and 1:50 for total phenolics and total proanthocyanidins measurements, respectively.

135 **2.6 HPLC analysis of anthocyanins**

136 Anthocyanin separation was performed according to the elution conditions, flow rate and
137 composition of the mobile phases previously reported by González-Centeno et al. (2017).

138 This HPLC methodology was conducted on an Agilent Nucleosil 100-5C18 (250 mm × 4.0
139 mm, 5 μm) column by using a Thermo-Accela HPLC instrument including a UV−vis
140 detector (Accela PDA detector), an autosampler (Accela autosampler), and a quaternary
141 pump (Accela 600 pump). Wines were filtered and injected directly, with no prior
142 treatment.
143 Anthocyanin 3-*O*-monoglucosides (delphinidin, Dp; cyanidin, Cy; petunidin, Pt; peonidin,
144 Pn; and malvidin, Mlv), as well as the acetylated and *p*-coumaroylated forms of Pn and
145 Mlv, were identified by comparison to injected external standards and/or previous results.
146 All anthocyanin analyses were performed in duplicate and results were expressed in mg of
147 Mlv-3-*O*-monoglucoside per liter of wine.

148 **2.7 Haloanisoles and halophenols of wines: extraction and gas chromatography**
149 **analysis**

150 Both haloanisoles and halophenols analyses were conducted in wines. Prior to gas-
151 chromatographic analyses, three liquid/liquid consecutive extractions were performed using
152 4, 2 and 2 mL of iso-hexane. Lindane solution (50 μL) was used as internal standard. The
153 organic fractions were all combined. Then, emulsion was broken thanks to a slow-agitation
154 by a magnetic stirrer and aqueous phase was progressively removed to get wine organic
155 extracts. All samples were extracted in duplicate.
156 Quantitative determination of both haloanisoles and halophenols in wines was adapted from
157 the gas chromatography OIV method (OIV, 2006). The equipment used for this analysis
158 consisted of an Agilent HP 5980 GC equipped with an electron capture detector (Agilent
159 Technologies, USA). Wine organic extracts (2 μL) were injected in split-splitless mode.
160 The experimental conditions were temperature set at 250 ºC for both injector and detector,
161 and 40 ºC for oven (programmed at 3 ºC/min to 160 ºC, and then at 5 ºC/min to 220 ºC, the
162 final step lasting 10 min); splitless time set at 30 s and split flow at 30 mL/min. The column
163 was a CP-Sil 5CB (PDMS, 50 m x 0.32 mm, 0.2 μm) and nitrogen was used as carrier gas.
164 Target compounds (TCA, 2,4,6-trichloroanisole; TeCA, 2,3,4,6-tetrachloroanisole; PCA,
165 pentachloroanisole; TBA, 2,4,6-tribromoanisole; TCP, 2,4,6-trichlorophenol; TeCP,

2,3,4,6-tetrachlorophenol; PCP, pentachlorophenol; TBP, 2,4,6-tribromophenol) were identified by comparing their retention times with those of the pure reference standards.

2.8 Volatile composition of wines: extraction and gas chromatography analysis

Woody and fruity aroma composition was determined by adapting the gas chromatography procedures described by Barbe and Bertrand (1996) and Antalick *et al.* (2010) respectively. The equipment used for woody and fruity aroma analyses consisted of an Agilent HP 5890 GC (Hewlett-Packard, Wilmington, DE, USA) coupled with a mass spectrometer (Agilent HP 5972, electron impact 70 eV, eMV = 2 kV), and an Agilent HP 7890 GC (Hewlett-Packard, Wilmington, DE, USA) coupled to a quadrupole mass spectrometer (Agilent HP 5975), respectively. Target compounds were identified by comparing their retention times and mass spectra with those of the pure reference standards. All samples were analyzed in duplicate. Calibration curves were established using pure reference standards analyzed under the same conditions than wine samples.

Woody aroma. For the identification of the target compounds, selected ions were *m/z* 99 for β-methyl-γ-octalactone, *m/z* 151 for vanillin, *m/z* 164 for eugenol, and *m/z* 83 for the internal standard (dodecan-1-ol).

Fruity aroma. The following ions were used to identify the target compounds: ethyl isobutyrate, *m/z* 116; ethyl propanoate and ethyl 2-methylbutyrate, *m/z* 102; ethyl butanoate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate and ethyl 3-methylbutyrate, *m/z* 88; isoamyl acetate, *m/z* 70; propyl acetate, *m/z* 61: and *m/z* 56 for isobutyl acetate and butyl acetate.

2.9 Sensory analysis

Sensory analysis was performed by a panel of 22 expert judges (5 males and 17 females), all research staff at the Institute of Vine and Wine Sciences of the University of Bordeaux, selected for their experience in wine tasting.

All evaluations were conducted in a standard sensory-analysis chamber (ISO-8589, 2010), equipped with individual tasting booths, where an uniform temperature (19-22 ºC) and

source of lighting, absence of noise and distracting stimuli were guaranteed. Wines (30 mL) were presented in standard black INAO glasses, covered with a Petri dish to minimize the escape of volatile components and randomly coded with three-digit numbers. The position of the samples was balanced in all sensory tests.

Training. To familiarize the panelists with TCA odor, all judges were trained over a period of two weeks. Training sessions were adapted from Cravero *et al.* (2015) and consisted of tests for elucidating the individual olfactory sensitivity to TCA. First, a TCA identification test was conducted. For this purpose, various TCA (CAS number 87-40-1, grade purity of 99%, Merck) solutions of the following concentrations 0, 0.1, 0.25, 0.5, 1.0, 2.0, 3.0, 4.0, 8.0 and 16.0 ng/L prepared in two different matrices: distilled water and red wine (100% Merlot 2016, Languedoc Roussillon), were evaluated. The selected wine had a bag-in-box closure system to reduce the risk of cork taint. The ten TCA concentrations were presented in ascending order (from 0 to 16 ng/L), preceded by control (water or wine), which was placed in the initial position. Judges were requested to indicate if the sample was perceived to be identical or not to the control. TCA detection test was repeated in triplicate for each matrix on three consecutive days.

Secondly, a series of three alternative forced-choice tests (ISO-13301, 2018) with eight ascending TCA concentrations (from 0.1 to 6 ng TCA/L) were carried out in red wine (100% Merlot 2016, Languedoc Roussillon). For each TCA concentration, three glasses were proposed: two controls and a third one containing the substance under test. Sensory panel was asked to identify the odd sample olfactory perceived as different from the others. This sensory test was repeated in triplicate on three consecutive days. Best Estimate Threshold (BET)-method was used to calculate the TCA threshold of the sensory panel. The individual BET was calculated as the geometric mean of the highest concentration missed and the next higher concentration (the lowest TCA concentration detected within a series of correct answers). The sensory panel BET was determined as the geometric mean of the individual BETs.

220 *Wine evaluation*. Triangle test (ISO-4120, 2007) was performed to determine whether the
221 panel was able to distinguish between contaminated wine and wines treated with film for 8,
222 24 and 48h. For this discriminatory test, the sensory panel attended six formal tasting
223 sessions (two per contaminated wine). In each session, contaminated wine from one out of
224 the three barrels considered was compared to the corresponding three film-treated wines
225 (after 8, 24 and 48h of wine-film contact). For each duo of wines, three glasses were
226 presented and judges were asked to indicate the one olfactory perceived as different from
227 the others (forced choice: even if s/he was not sure). The presentation order was
228 randomized, corresponding to the six possible presentation orders.
229 Descriptive sensory analysis was also performed to assess the sensory profile of all wines.
230 Samples were first evaluated orthonasally. Olfactory descriptors considered were fruity,
231 overall woody, corky and vegetal. Then, after a short break, both bitterness and astringency
232 attributes were also evaluated. The sensory panel was asked to rate the intensity level of all
233 descriptors on a line scale (10 cm) ranging from 'absence' (note 0) to 'maximum intensity'
234 (note 10). Results of each descriptor were then expressed as the mean value of all the
235 judges from two formal tasting sessions.

236 **2.10 Additional experiment to control the impact of the plastic film on flavan-3-ol**
237 **composition and fruity character of wines**
238 In order to check the real impact of the plastic film on the flavan-3-ol profile and the fruity
239 character of wine, an additional experiment was conducted. A HAs-free wine (70%
240 *Cabernet Sauvignon*, 30% *Merlot*, 24-months of barrel ageing) was considered as control
241 and supplemented with three different TCA levels corresponding to the initial polluted
242 wines from barrels A (1.0 ng TCA/L wine), B (3.0 ng TCA/L wine) and C (9.1 ng TCA/L
243 wine). For this purpose, a stock solution of TCA (CAS number 87-40-1, grade purity of
244 99%, Merck) was prepared in EtOH (1 g/L) and, then, diluted for use. Film treatment was
245 conducted in all cases at a dose of 20 m^2 film/hL wine.
246 *Flavan-3-ol composition of wines*. To evaluate the impact of the film treatment on the
247 flavan-3-ol profile, all three supplemented wines were film-treated for a length determined

248 by the tasters' capacity to find significant differences at the triangle tests between the
249 untreated and film-treated wines of *Wine evaluation* (see 3.6 Sensory analysis section).
250 Specifically, wine supplemented with 1.0 ng TCA/L was film-treated during 8h; wine
251 supplemented with 3.0 ng TCA/L, during 48h; and wine supplemented with 9.1 ng TCA/L,
252 during 24h.
253 Monomeric and oligomeric flavan-3-ols were quantified in control wine, as well as in the
254 three supplemented and film-treated wines, on a Thermo-Finnigan Surveyor HPLC system.
255 The flow rate, elution conditions, composition of mobile phases and column characteristics
256 were adapted from González-Centeno et al. (2012). Wines were filtered and injected
257 directly in triplicate. Results were expressed in mg of (+)-catechin/L wine.
258 *Fruity character of wines*. Four different modalities were considered for each TCA
259 supplementation level: I. control wine (not supplemented and not film-treated), II.
260 supplemented wine, III. film-treated wine (not supplemented), and IV. supplemented and
261 film-treated wine. The length of the film treatment for modalities III and IV corresponded
262 once again to that for what tasters found significant differences at the triangle tests between
263 the untreated and the film-treated wines of *Wine evaluation* (see 3.6 Sensory analysis
264 section).

265 Triangle test (ISO-4120, 2007) was carried out to evaluate whether the panel was able to
266 distinguish between: a) modalities II and IV (to confirm the obtained results about the film
267 treatment efficacy); and b) modalities I and III (to evaluate both the film sorption of esters,
268 and the resulting effect on fruity aroma perception). If difference was perceived at the
269 triangle test, bilateral paired comparison test (ISO-5495, 2007) was also performed to
270 identify to what sensory descriptors judges related that difference. HAs content and fruity
271 aroma profile of all four modalities for the three levels of TCA contamination were also
272 analyzed by chromatography.

273 **2.11 Statistical analysis**

All experimental results were reported as mean values with their corresponding standard deviations. Statistical analysis was performed by the statistical package R version 3.5.0 (R Foundation for Statistical Computing, Wien, Austria). Normality and homocedasticity of the residuals were evaluated for all parameters, by using the Shapiro–Wilk test and Levene's test, respectively. When populations were distributed normally and presented homogeneity in variance, the parametric ANOVA and Tukey tests were used to evaluate the existence and degree of significant differences. If populations were not distributed normally and/or presented heterogeneity in variance ANOVA was replaced by the nonparametric Friedman test. Differences at $p \leq 0.05$ were considered to be statistically significant.

The results of the sensory triangle tests were analyzed by the probability theory that the number of right answers follows a binomial distribution (n, $p = 1/3$ for triangle test), where n is the panel size. Wines were considered as differently perceived for a probability lower than 5%.

3. Results and discussion

3.1 Haloanisoles and halophenols content of wines

Both haloanisoles (HA) and halophenols (HP) content of wines are shown in Table 1. The presence of these compounds in the initial wines, non-treated with the film, proved the contamination of the corresponding barrels. Each one presented a different contamination level, being the untreated wine from barrel C the most contaminated one, with a TCA content of 9.1 ± 0.2 ng/L wine. Untreated wine from barrel B showed an intermediate TCA contamination (3.0 ± 0.1 ng/L wine) and that from barrel A just presented some traces of TCA (≤ 1.0 ng/L wine).

As observed, the use of the plastic film reduced significantly ($p < 0.05$) the TCA content of the initial wines. This decrease became more noticeable as the contact time film-wine increased. In the case of barrel B, after 8h of film-treatment TCA concentration lessened up to 47% of the initial content. A longer treatment of 24h and 48h led to a reduction of 73% and 83% of the TCA contamination, respectively. In the case of barrel C, a slightly higher decrease of the TCA level (57%) was observed after the first 8h of film-treatment. Meanwhile, similar values were obtained after 24h (reduction of 75% initial TCA content) and 48h (diminution of 81% initial TCA concentration) of film-wine contact. In the case of barrel A, TCA decontamination was no quantifiable (values under the limit of quantification, 0.5 ng/L), but it is important to point out that there was a diminution of the TCA content up to no detection in wine after 48h of film-treatment.

HAs have very low detection thresholds in alcoholic solution (in the range of ng/L), which make their mouldy, musty, earthy or 'wet cardboard' off-flavours easily recognizable (Callejón, Ubeda, Ríos-Reina, Morales, & Troncoso, 2016). In the case of TCA, published detection threshold may vary considerably depending not only on panel expertise, sensitivity and training, but also on wine style and matrix (Mazzoleni & Maggi, 2007). Specifically, the most extended values of TCA perception threshold in red wine range between 1.5 and 3.0 ng/L (Grainger & Tattersall, 2016). As observed in Table 1, at the end

315 of the film treatment, wines presented TCA contents around the bottom limit of that range,
316 or even much lower values.

317 TBA was not detected in any of the wine samples analyzed, while no quantifiable amounts
318 of TeCA and/or PCA were found in the three untreated wines. As observed in Table 1, the
319 plastic film was able to eliminate the TeCA from wines of barrels B and C up to non-
320 detection.

321 HAs are considered among the most non-polar compounds present in wine. For this reason,
322 hydrophobic materials such as cork particles and plastics are effective at diminishing their
323 levels from contaminated wines (Waterhouse, Sacks, & Jeffery, 2016).

324 With regard to the halophenols, no quantifiable amounts of TeCP were found in any wine
325 sample. The film-treatment significantly decreased the PCP and TBP contamination of
326 wines to concentrations under the limit of quantification (3.0 ng/L for both halophenols)
327 and up to non-detection, respectively. Meanwhile, it did not seem to be very effective to
328 reduce/eliminate their TCP content. As for the HAs, untreated wine from barrel C presented
329 the highest TCP level (64.3 ng/L wine), followed by untreated wines from barrels B (11.8
330 ng/L wine) and A (8.1 ng/L wine), in this order. After 48h of wine-film contact, TCP
331 contamination only diminished in a 33% (barrel A), 6% (barrel B) and 11% (barrel C) from
332 initial values. Taking into account that HPs are not volatile compounds and that under
333 bottled wine conditions they may not become the corresponding HAs, the presence of TCP
334 still after the film treatment is not a matter of concern with regard to the cork taint off-
335 flavour.

336 **3.2 Oenological and chromatic parameters in wines**

337 The comparison of initial TCA-contaminated wines (untreated) and the corresponding film-
338 treated wines suggests that their basic structure is virtually identical. All of them presented
339 the same oenological characteristics, i.e., pH of 3.5, a density of 992 g/L wine, an alcohol
340 content of 14.0%, a titratable acidity of 3.7 g tartaric acid/L, a volatile acidity of 0.7 g
341 tartaric acid/L, a glucose/fructose ratio of 3.1, a total polyphenol index of 65 ± 1 and malic,

lactic and tartaric acid contents of 0.4, 0.8 and 2.2 g/L wine, respectively. Thus, the use of the plastic film to eliminate/reduce both HA and HP content in wines did not influence their oenological parameters, and this regardless of the contact time of the film-treatment.

Chromatic characteristics (color intensity, hue and yellow, red and blue components) of all wines analyzed are depicted in Figure 1. A priori, no chromatic parameter really changed because of the film treatment and/or the contact time film-wine. Nevertheless, some differences between untreated and film-treated wines, and even among wines treated with film for different contact times, were found to be statistically significant ($p < 0.05$). These differences ($\leq 6\%$ with regard to the corresponding untreated wine) were mainly attributed to the highly reproducibility of the absorbance measurements, but they were not visually perceived by any taster during sensory analysis.

3.3 Total phenolic, proanthocyanidin and anthocyanin content

Table 2 shows the total phenolic, proanthocyanidin and anthocyanidin contents of all untreated and film-treated wines analyzed in the present study. After the film-treatment to remove HA and HP from wines, total phenolic and total proanthocyanidin values remained constant for wines from barrels B and C ($p > 0.05$), regardless of the contact time film-wine. Meanwhile, in the case of barrel A, a slightly decrease (4.4%) of total phenolics was observed with regard to the untreated wine after 48h of film-treatment.

With regard to the anthocyanin results, film-treated wines from barrels A and C displayed a little but significant rise of total anthocyanins at 48h and 24h of contact, respectively ($p < 0.05$). This increase suggested that the plastic film might absorb certain wine components that anthocyanins are used to combine. In fact, anthocyanins are the main pigments present in young red wines, being responsible for their intense red color. During oak wood wine aging anthocyanins can yield polymeric pigments by their reaction with flavanols (directly or mediated by aldehydes). Moreover, A-type vitisins (the main pyranoanthocyanins found in red wines) can also react with other wine components giving origin to polymeric pigments with different colors ranging from yellow to turquoise blue.

According to these results, it may be globally stated that the use of the plastic film to eliminate/reduce both HAs and HPs content in wines did not impact significantly their phenolic, proanthocyanidin and anthocyanin contents up to 24h of film-treatment.

3.4 Anthocyanin composition of wines

Since some evolution of the total anthocyanin content was observed during the film treatment, the anthocyanin profile of both untreated and film-treated wines was also analyzed to get in-depth information. The total anthocyanin content of all wines, calculated by adding up the individual concentration of each anthocyanin compound, ranged from 38.5 to 45.1 mg Mlv/L wine. The same anthocyanin profile was observed for both untreated and film-treated wines, malvidin-3*O*-glucoside being the most abundant component and accounting for 29–32% of the total anthocyanin fraction. In all cases, delphinidin-3*O*-glucoside was the second main anthocyanin (~15%), followed by similar concentrations of both petunidin and peonidin (~13%), and then, the acetyl form of malvidin (~11%), cyanidin (~9%) and the acetyl form of peonidin (~8%), in that order (Table 3).

Film-treatment length did not lead to significant differences ($p > 0.05$) among film-treated wines from each barrel for any individual anthocyanin. However, when compared to the untreated wines, film-treated wines presented slightly greater concentrations ($p < 0.05$) of some anthocyanins after 8h of film contact (2 –14%). Malvidin-3*O*-glucoside and delphinidin-3*O*-glucoside were the main responsible of these increases. This observation corroborates the results derived from the total anthocyanin analysis of wines from barrels A and C and may be explained by the same chemical approach: a potential film absorption of certain carbonyl compounds which tend to combine anthocyanins.

3.5 Volatile composition of wines

3.5.1 Woody aroma

The evolution of the main direct contributors to the overall woody aroma (whiskeylactones, eugenol, vanillin) during film-treatment is also described in Table 4. Woody aroma profile of all three wines remained constant throughout the film-treatment. Only a decrease of

396 vanillin (13 – 26%) content was observed in wine from barrel B beyond 8h of wine-film
397 contact. Meanwhile, it is important to point out that vanillin content remained at
398 concentrations well above its perception threshold (320 μg/L) (Boidron, Chatonnet, &
399 Pons, 1988), regardless of the length of the film-treatment.

400 In any case, the concentration of both *cis*- and *trans*-whiskeylactones, main responsible of
401 the coconut, woody and oak-like notes of wine aged in barrels, and the eugenol content,
402 related to spicy and smoked flavors, were not modified by the film-treatment in any of the
403 wines considered.

404 Globally, it may be concluded that the plastic film did not sorb the oak woody volatiles,
405 since the woody aroma profile was not significantly impacted by the film-treatment used to
406 eliminate/reduce both HAs and HPs content in wines.

407 *3.5.2 Fruity aroma*

408 The evolution of the fruity aroma profile during film-treatment is also depicted in Table 4.
409 Among the three main families of esters contributing to the fruity character of red wine, the
410 concentrations of both higher alcohol acetates and ethyl esters branched acids, remained
411 practically constant during the whole film treatment of wines.

412 Only the ethyl esters of straight-chain fatty acids displayed a significant reduction
413 throughout the film-treatment ($p < 0,05$). These volatiles, responsible for pineapple, plum,
414 apple and blackberry aromatic notes, decreased in a higher extent as the contact time film-
415 wine increased. Specifically, ethyl hexanoate experimented a lessening from 17% to 26%
416 compared to the untreated wine. In the case of ethyl octanoate, ethyl decanoate and ethyl
417 dodecanoate, the decline percentages were much higher. Losses accounted for ≥ 31% of
418 their initial contents after only 8h of wine-film contact. A longer treatment of 48h led to a
419 reduction from up to 82% of their initial concentrations. Thus, the plastic film seemed to
420 display a selective sorption of those four ethyl esters.

421 As previously noted in the literature, both concentration and hydrophobicity of aroma
422 compounds may govern their affinity for plastic films (Dury-Brun, Chalier, Desobry, &

Voilley, 2008). According to the apolar nature of the plastic film used, it is well known that i. aromatic volatiles are easily sorbed, in particular, the hydrophobic ones (Dombre, Rigou, Wirth, & Chalier, 2015); and that ii. the higher the hydrophobicity in the chemical family, the greater the sorption coefficient (Peyches-Bach, Moutounet, Peyron, & Chalier, 2009). Among the three ester families quantified, that of ethyl esters of straight-chain fatty acids presents very hydrophobic molecules. This particularity may justify their selective sorption by the plastic film.

The question remains as to whether the decline of these fruity volatiles, even if present at sub-threshold concentrations, may impact both the expression and perception of red wine fruity aroma, due to their potential synergism, modulation and/or enhancement phenomena of fruity character (Lytra, Tempere, de Revel, & Barbe, 2012; Lytra, Tempere, Le Floch, de Revel, & Barbe, 2013). In order to answer this query, a second sensory analysis experiment has been performed (see *Wine evaluation – Experiment II* sub-section at 2.9 Sensory analysis section).

3.6 Sensory analysis

After training sessions, all judges were able to clearly identify the presence of TCA in red wine. Moreover, the BET results showed that the sensory panel may detect TCA in red wine at 1.2 ng TCA/L. This value is in quite agreement with the odor detection threshold of TCA in red wine (0.9 ng TCA/L) previously reported by Teixeira *et al.* (2006).

Wine evaluation. According to the results of the triangle test, sensory panel significantly distinguished between untreated wines and film-treated wines after 8h, 24h and 48h of film contact for barrels A (52% of correct answers, $p \leq 0.007$), C (50% of correct answers, $p \leq 0.016$) and B (50% of correct answers, $p \leq 0.016$), respectively. Specifically, these film-treatments corresponded to a reduction of TCA pollution under the limit of quantification (0.5 ng/L) in the case of barrel A, and a decrease of 75% and 83% of the initial TCA content of the wine for barrels C and B, respectively.

449 It was maybe expected that judges significantly distinguish film-treated from untreated
450 wine at 24h for the wine presenting the intermediate TCA pollution (barrel B) and at 48h
451 for the wine with the highest TCA level (barrel C), and not vice versa. Nevertheless, the
452 TCA level of the untreated wine from barrel B is so closed to the detection threshold of this
453 unpleasant volatile that it might slow the differentiation down. In the case of barrel C, the
454 untreated wine is so polluted that a shorter treatment was enough to perceive the TCA
455 decrease.
456 In the case of barrel A, even if the selected panel significantly distinguished the 8h film-
457 treated wine from the contaminated initial wine, differences were not significantly
458 associated to any of the organoleptic attributes considered during the descriptive sensory
459 analysis ($p > 0.05$). This behavior may be explained because the pollution levels of both
460 untreated and film-treated wines from barrel A (< 1.0 ng/L wine) were very close or under
461 the TCA threshold of the selected panel (BET = 0.8 ng/L wine). It is important to note that,
462 as depicted in Figure 2A, after 8h of film contact judges perceived wine with slightly higher
463 fruity notes than the untreated one. Even if it was not statistically significant ($p > 0.05$),
464 these results confirm the observations of Tempere *et al.* (2017) regarding the masking
465 effect of TCA on fruity notes at infra-threshold concentrations. Their study provides
466 experimental confirmation that non-perceptible concentrations of TCA may also negatively
467 influence the perceived olfactory quality of a wine.
468 In the case of barrel B, different perception of untreated and 48h film-treated wines was
469 related to the fruity, overall woody and corky descriptors (Figure 2B). Specifically, wine
470 from barrel B treated with the plastic film during 48h was described as fruitier and woodier,
471 and less corky than the untreated wine. As previously noted, no increase of the fruity and/or
472 woody volatile content was observed during the film treatment (Table 4). Thus, according
473 to the judges' perception, both fruity and woody notes just appeared because of the 83%
474 decrease of the initial TCA contamination after 48h of film-treatment, and consequently, an
475 important reduction of the corky aroma, which was acting as a potent masking agent of
476 pleasant aromas.

In the case of barrel C, sensory differences between untreated and 24h film-treated wines were associated to the fruity and corky olfactory descriptors, as well as to both bitterness and astringency attributes. Just like wine from barrel B, the higher fruity character of the film-treated wine was directly linked to the significant 75% decrease of the initial TCA contamination. Furthermore, as observed in Figure 2C, untreated wine was described as more bitter and astringent ($p < 0.05$) than the corresponding film-treated wines. Judges, even if they are trained, do not always describe bitter and astringent perceptions with the expected descriptors. When consumers like the wines, they tend to not use the term 'bitter' as a descriptor. It is normally used to express dislike and is usually associated with acid and astringent sensory characteristics. On the other hand, consumers who like astringent wines described them as having 'a lot of character' or 'a long aftertaste' (Chira, Schmauch, Saucier, Fabre, & Teissedre, 2009). As the wines treated with the film were perceived as fruitier than the non-treated wines, judges characterized them instantaneously as less astringent and bitter.

It is important to point out that all film-treated wines (from barrels B and C) were significantly perceived as less corky than the corresponding initial untreated wines, regardless of the length of the film treatment. These results suggested that the plastic film was able to improve the organoleptic quality of wines contaminated with HAs, by reducing the corky notes and increasing the perception of their overall woody and/or fruity aromas.

3.7 Impact of the film treatment on flavan-3-ol composition and fruity character of wines

Flavan-3-ol composition of wines. As previously described in section 3.3, total proanthocyanidin content of film-treated wines did not change significantly compared to untreated wine. The analysis of the flavan-3-ol profile performed in the additional experiment corroborated those results, since regardless of the TCA supplementation level applied, all film-treated wines presented the same flavan-3-ol content and profile than control wine. As observed in Table S2 (at the Supplementary material section), neither monomers or dimers have not been affected by the film treatment. Thus, this additional

505 experiment confirmed that the film-treatment of wines did not impact their flavan-3-ol
506 profile.
507 *Fruity character of wines*. Even if film-treated wines presented a significant reduction of
508 some fruity volatiles, they were described as fruitier than the untreated wines. The
509 additional sensory experience aimed to check the real impact of the film treatment on fruity
510 aroma perception.
511 Results from the triangle test for modalities II (supplemented wine) and IV (supplemented
512 and film-treated wine) corroborated the results obtained in the present research about the
513 great efficacy of the film treatment (wine supplemented with 1.0 ng TCA/L, 58% of correct
514 answers, $p \leq 0.09$; wines supplemented with 3.0 and 9.1 ng TCA/L, 54% of correct
515 answers, $p \leq 0.025$). At the three levels of TCA supplementation, judges were able to
516 distinguish significantly between the wine untreated (mod. II) and the film-treated one
517 (mod. IV). In all cases, this differentiation was associated to the lowest corky and greater
518 fruity notes ($p < 0.05$) of film-treated wines (mod. IV).
519 At a chemical level, the film treatment reduced significantly the ester content (Table S3, at
520 the Supplementary material section), but also the TCA supplementation (up to no detection
521 for wines supplemented with 1.0 and 3.0 ng TCA/L, and a reduction of 83% after 24h of
522 film treatment for wine supplemented with 9.1 ng TCA/L). Losses of fruity volatiles by
523 film sorption reached again the highest values for ethyl esters of straight-chain fatty acids,
524 surely due to their greater hydrophobicity.
525 When comparing modalities I (control wine) and III (film-treated wine), both without TCA
526 supplementation, the triangle test revealed that the film treatment had not a significant
527 impact on fruity perception. Regardless of the contact time wine-film, judges were not able
528 to differentiate between control wine and film-treated wine ($p > 0.05$). Thus, even if a
529 significant decrease of certain esters was observed due to the film treatment (Table S3), it
530 did not influence the perception of the fruity character of the wine.

4. Conclusions

The film treatment i. allowed to gradually remove TCA from polluted wine (81 – 83 % after 48h of wine-film contact); ii. did not impact neither colour attributes, nor both total phenolic and tannin contents, and the woody aroma profile; iii. slightly increased anthocyanin content beyond 24h of wine-film contact and absorbed significantly only certain esters; iv. nonetheless, did not influence the fruity perception of wines; and v. reduced significantly the corky notes, regardless of the contact time (8h, 24h or 48h).

Overall, the present research highlighted that this film treatment is highly efficient to improve the organoleptic quality of wines contaminated with HAs, by reducing the cork taint and increasing their overall fruity aroma, without highly impacting their chromatic parameters, phenolic and aromatic composition.

Acknowledgements. The authors gratefully acknowledge all the judges who participated in the sensory analyses.

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659

Figure captions

Figure 1. Chromatic parameters of untreated and film-treated wines. (**A**) colour intensity (CI) and hue; (**B**) yellow, red and blue components (%).

Figure 2. Descriptive sensory evaluation of untreated wines and film-treated wine perceived as significantly different from untreated wine at the triangle test, for barrel A (**A**), barrel B (**B**) and barrel C (**C**). * Significant at $p < 0.05$.

Figure 1

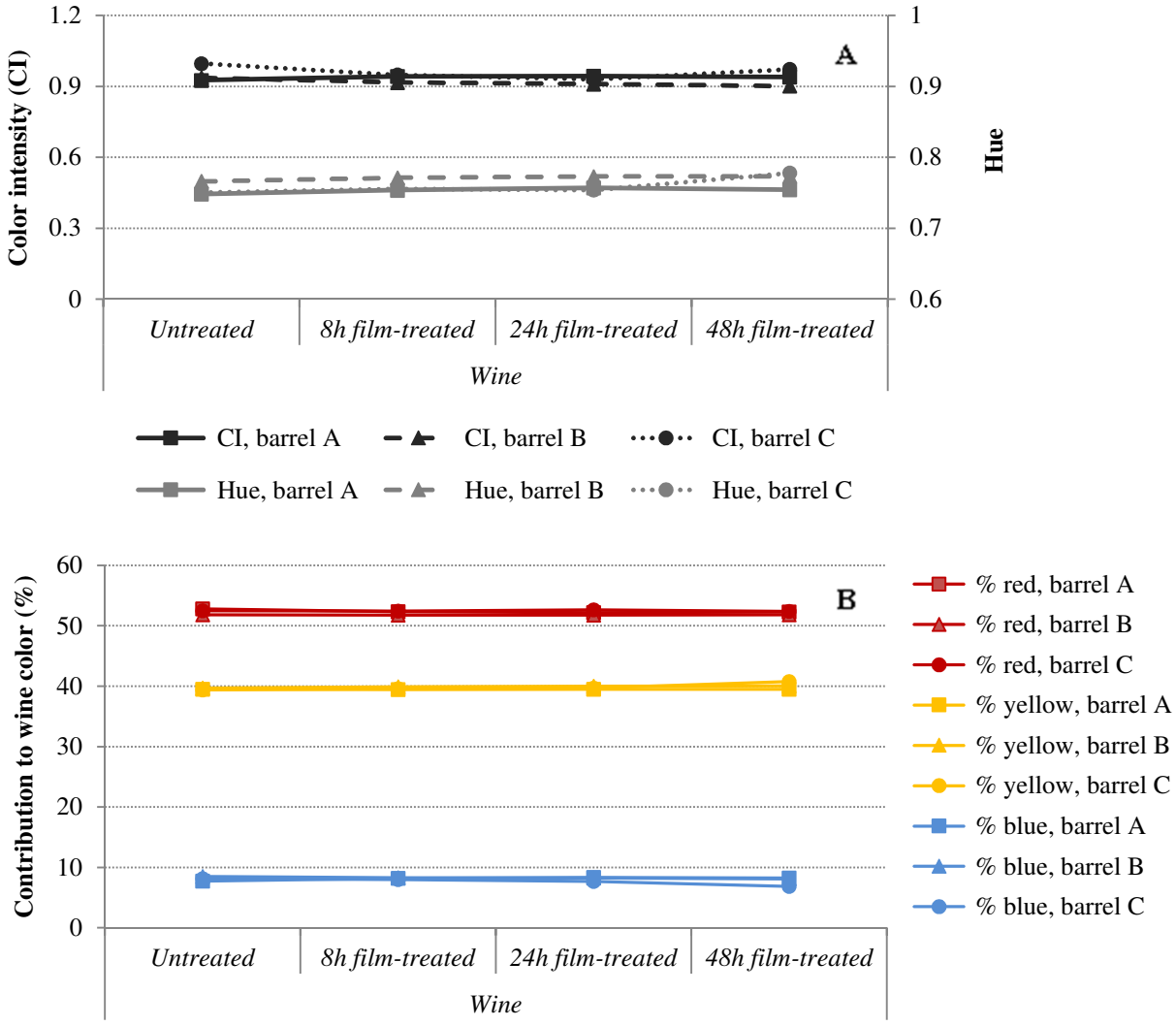
A
Color intensity (CI)
Hue
1.2
0.9
0.6
0.3
0
1
0.9
0.8
0.7
0.6
Untreated
8h film-treated
24h film-treated
48h film-treated
Wine
CI, barrel A
CI, barrel B
CI, barrel C
Hue, barrel A
Hue, barrel B
Hue, barrel C
B
Contribution to wine color (%)
60
50
40
30
20
10
0
% red, barrel A
% red, barrel B
% red, barrel C
% yellow, barrel A
% yellow, barrel B
% yellow, barrel C
% blue, barrel A
% blue, barrel B
% blue, barrel C
Untreated
8h film-treated
24h film-treated
48h film-treated
Wine

Figure 2

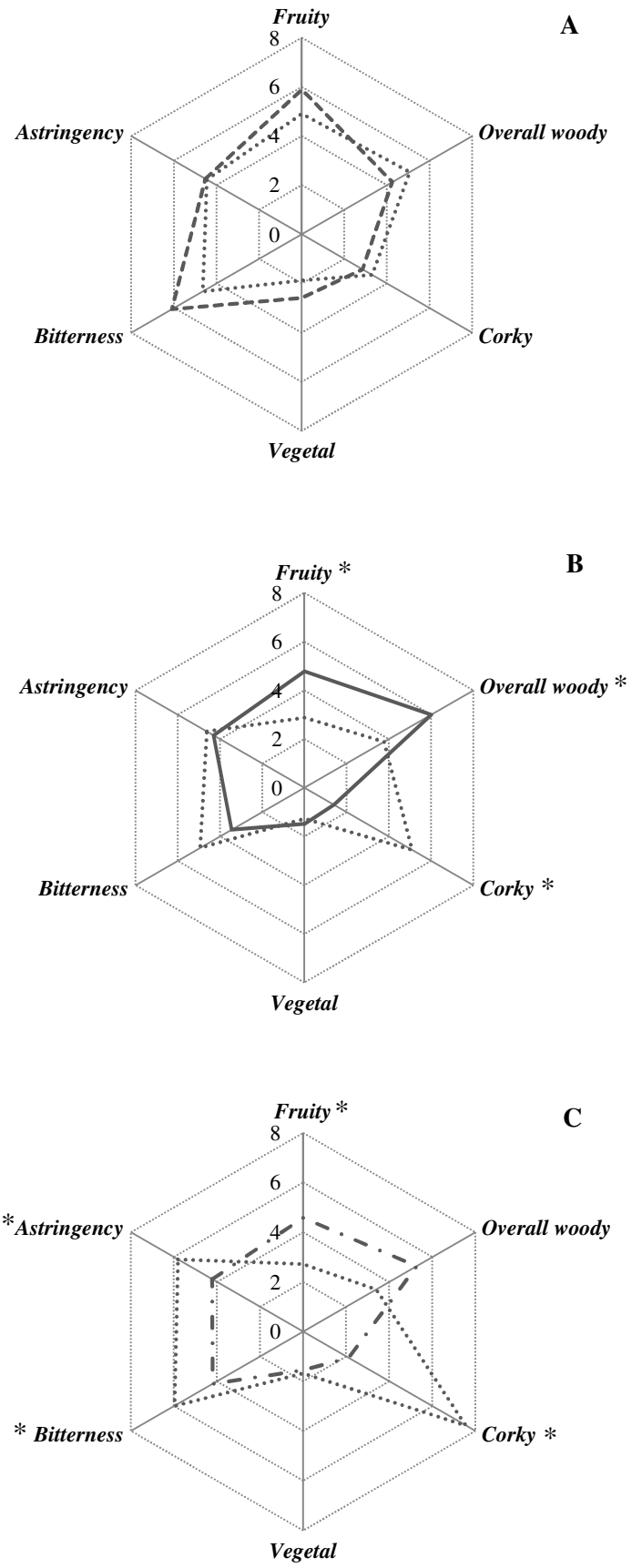
A
Fruity
8
6
4
2
0
Overall woody
Corky
Vegetal
Bitterness
Astringency
B
Fruity *
Overall woody *
Corky *
Vegetal
Bitterness
Astringency
C
Fruity *
Overall woody
Corky *
Vegetal
* Bitterness
*Astringency
Untreated wine
8h film-treated wine
24h film-treated wine
48h film-treated wine

Table 1. Haloanisoles and halophenols evolution of untreated and film-treated wines from barrels A, B and C.

	Haloanisoles				Halophenols			
	TCA	**TeCA**	**PCA**	**TBA**	**TCP**	**TeCP**	**PCP**	**TBP**
Barrel A								
Untreated wine	1,0	*< LoQ*	*< LoQ*	*nd*	8,1	*< LoQ*	3,9	*< LoQ*
8h film-treated wine	*< LoQ*	*< LoQ*	*< LoQ*	*nd*	8,6	*< LoQ*	3,1	*< LoQ*
24h film-treated wine	*< LoQ*	*< LoQ*	*< LoQ*	*nd*	5,6	*< LoQ*	3,1	*nd*
48h film-treated wine	*nd*	*< LoQ*	*< LoQ*	*nd*	5,4	*< LoQ*	*< LoQ*	*nd*
Barrel B								
Untreated wine	3,0	*< LoQ*	*nd*	*nd*	11,8	*< LoQ*	5,3	*< LoQ*
8h film-treated wine	1,6	*nd*	*nd*	*nd*	12,3	*< LoQ*	*< LoQ*	*< LoQ*
24h film-treated wine	0,8	*nd*	*nd*	*nd*	13,8	*< LoQ*	*< LoQ*	*< LoQ*
48h film-treated wine	0,5	*nd*	*nd*	*nd*	11,1	*< LoQ*	*< LoQ*	*nd*
Barrel C								
Untreated wine	9,1	*< LoQ*	*nd*	*nd*	64,3	*< LoQ*	*< LoQ*	*< LoQ*
8h film-treated wine	3,9	*nd*	*nd*	*nd*	59,7	*< LoQ*	*< LoQ*	*< LoQ*
24h film-treated wine	2,3	*nd*	*nd*	*nd*	63,9	*< LoQ*	*< LoQ*	*< LoQ*
48h film-treated wine	*1,7*	*nd*	*nd*	*nd*	57,4	*< LoQ*	*< LoQ*	*nd*

TCA, 2,4,6-trichloroanisole. TeCA, 2,3,4,6-tetrachloroanisole. PCA, pentachloroanisole. TBA, 2,4,6-tribromoanisole. TCP, 2,4,6-trichlorophenol. TeCP, 2,3,4,6-tetrachlorophenol. PCP, pentachlorophenol. TBP, 2,4,6-tribromophenol. LoQ, limit of quantification. nd, not detected. All results were expressed in ng/L wine.

Table 2. Total phenolic, total proanthocyanidin, and total anthocyanin contents of untreated and film-treated wines from barrels A, B and C.

	Total phenolics[a]	**Total proanthocyanidins**[b]	**Total anthocyanins**[c]
Barrel A			
Untreated wine	2891 ± 36 *a*	3,5 ± 0,2 *b*	133,4 ± 4,0 *b*
8h film-treated wine	2876 ± 45 *a*	3,7 ± 0,1 *b*	138,8 ± 4,6 *ab*
24h film-treated wine	2874 ± 87 *a*	4,1 ± 0,1 *a*	147,0 ± 3,4 *ab*
48h film-treated wine	2766 ± 36 *b*	3,6 ± 0,1 *b*	149,5 ± 9,3 *a*
Barrel B			
Untreated wine	2781 ± 77 *a*	3,7 ± 0,2 *a*	171,9 ± 3,4 *a*
8h film-treated wine	2782 ± 125 *a*	4,1 ± 0,2 *a*	177,2 ± 5,6 *a*
24h film-treated wine	2750 ± 68 *a*	3,8 ± 0,3 *a*	175,1 ± 7,6 *a*
48h film-treated wine	2852 ± 57 *a*	3,6 ± 0,6 *a*	165,1 ± 2,2 *a*
Barrel C			
Untreated wine	2847 ± 134 *a*	3,7 ± 0,2 *a*	144,9 ± 10,2 *b*
8h film-treated wine	2814 ± 122 *a*	3,5 ± 0,3 *a*	160,2 ± 7,2 *ab*
24h film-treated wine	2809 ± 117 *a*	3,6 ± 0,1 *a*	171,1 ± 5,5 *a*
48h film-treated wine	2852 ± 67 *a*	3,6 ± 0,2 *a*	169,6 ± 3,8 *a*

All results are reported as mean values ± standard deviation. [a] Total phenolics expressed as mg gallic acid/L wine. [b] Total proanthocyanidins expressed as g tannins/L wine. [c] Total anthocyanins expressed as mg malvidin/L wine. For each spectrophotometric measurement, lower case letters a–b show significant differences between untreated and film-treated wines from each barrel separately ($p < 0.05$).

Table 3. Anthocyanin profile of untreated and film-treated wines from barrels A, B and C.

	Barrel A				Barrel B				Barrel C			
	Untreated wine	**8h film-treated wine**	**24h film-treated wine**	**48h film-treated wine**	**Untreated wine**	**8h film-treated wine**	**24h film-treated wine**	**48h film-treated wine**	**Untreated wine**	**8h film-treated wine**	**24h film-treated wine**	**48h film-treated wine**
Dp-3O-glc	5,8 ± 0,1 *b*	6,0 ± 0,1 *a*	6,1 ± 0,0 *a*	6,1 ± 0,0 *a*	6,5 ± 0,1 *a*	6,7 ± 0,2 *a*	6,7 ± 0,0 *a*	6,7 ± 0,0 *a*	5,6 ± 0,1 *c*	6,1 ± 0,0 *b*	6,3 ± 0,0 *a*	6,2 ± 0,0 *a*
Cy-3O-glc	3,7 ± 0,0 *b*	3,8 ± 0,0 *a*	3,8 ± 0,0 *a*	3,8 ± 0,0 *a*	3,8 ± 0,1 *a*	3,9 ± 0,0 *a*	3,9 ± 0,0 *a*	3,9 ± 0,0 *a*	3,7 ± 0,0 *a*	3,8 ± 0,0 *a*	3,8 ± 0,0 *a*	3,8 ± 0,0 *a*
Pt-3O-glc	5,4 ± 0,0 *a*	5,4 ± 0,0 *a*	5,4 ± 0,1 *a*	5,4 ± 0,0 *a*	5,7 ± 0,0 *a*	5,9 ± 0,1 *a*	5,9 ± 0,1 *a*	5,9 ± 0,2 *a*	5,1 ± 0,0 *b*	5,5 ± 0,0 *a*	5,4 ± 0,0 *a*	5,5 ± 0,1 *a*
Pn-3O-glc	5,3 ± 0,1 *a*	5,5 ± 0,0 *a*	5,4 ± 0,2 *a*	5,4 ± 0,1 *a*	5,6 ± 0,1 *a*	5,7 ± 0,1 *a*	5,7 ± 0,1 *a*	5,8 ± 0,0 *a*	5,2 ± 0,1 *b*	5,5 ± 0,0 *a*	5,5 ± 0,0 *a*	5,5 ± 0,0 *a*
Mlv-3O-glc	11,8 ± 0,1 *b*	12,7 ± 0,3 *a*	12,8 ± 0,1 *a*	12,6 ± 0,1 *a*	13,7 ± 0,1 *b*	14,5 ± 0,0 *a*	14,4 ± 0,1 *a*	14,4 ± 0,2 *a*	11,3 ± 0,1 *c*	12,8 ± 0,0 *b*	13,1 ± 0,0 *a*	12,9 ± 0,1 *b*
Pn-3O-acglc	3,4 ± 0,0 *a*	3,5 ± 0,0 *a*	3,4 ± 0,0 *a*	3,4 ± 0,0 *a*	3,5 ± 0,0 *a*	3,5 ± 0,0 *a*	3,5 ± 0,0 *a*	3,5 ± 0,0 *a*	3,4 ± 0,0 *b*	3,5 ± 0,0 *a*	3,5 ± 0,0 *a*	3,4 ± 0,0 *ab*
Mlv-3O-acglc	4,4 ± 0,0 *a*	4,4 ± 0,1 *a*	4,4 ± 0,0 *a*	4,4 ± 0,0 *a*	4,7 ± 0,0 *b*	4,8 ± 0,1 *ab*	4,8 ± 0,1 *ab*	4,9 ± 0,0 *a*	4,3 ± 0,1 *b*	4,4 ± 0,0 *ab*	4,4 ± 0,1 *ab*	4,5 ± 0,0 *a*

All results are reported as mean values ± standard deviation and expressed in mg malvidin/L wine. Glc, monoglucoside; acgld, 6"-acetylglucoside; Dp, delphinidin; Cy, 3yaniding; Pt, petunidin; Pn, peonidin; Mlv, malvidin. For each individual anthocyanin, lower case letters a−c show significant differences between untreated and film-treated wines from each barrel separately ($p < 0.05$).

Table 4. Fruity and woody aroma evolution of untreated and film-treated wines from barrels A, B and C.

	Barrel A				Barrel B				Barrel C			
	Untreated wine[a]	8h film-treated wine[b]	24h film-treated wine[b]	48h film-treated wine[b]	Untreated wine[a]	8h film-treated wine[b]	24h film-treated wine[b]	48h film-treated wine[b]	Untreated wine[a]	8h film-treated wine[b]	24h film-treated wine[b]	48h film-treated wine[b]
Fruity aroma												
Ethyl esters of straight-chain fatty acids												
Ethyl propanoate	262,4 ± 15,2	*ns*	*ns*	*ns*	297,0 ± 15,2	*ns*	*ns*	*ns*	283,0 ± 18,5	*ns*	*ns*	*ns*
Ethyl butanoate	123,8 ± 3,6	*ns*	*ns*	*ns*	132,4 ± 8,1	*ns*	*ns*	*ns*	129,3 ± 9,3	*ns*	*ns*	*ns*
Ethyl hexanoate	141,9 ± 5,6 *a*	*ns*	- 21% *b*	- 21% *b*	148,4 ± 6,1 *a*	- 17% *b*	- 19% *b*	- 26% *b*	148,3 ± 9,9 *a*	*ns*	- 19% *b*	- 24% *b*
Ethyl octanoate	115,3 ± 6,5 *a*	- 48% *b*	- 69% *c*	- 76% *c*	118,4 ± 10,2 *a*	- 54% *b*	- 70% *c*	- 78% *d*	115,9 ± 8,1 *a*	- 42% *b*	- 63% *c*	- 73% *d*
Ethyl decanoate	40,3 ± 1,8 *a*	- 48% *b*	- 62% *c*	- 80% *d*	32,9 ± 0,2 *a*	- 58% *b*	- 77% *c*	- 82% *d*	41,9 ± 0,1 *a*	- 51% *b*	- 72% *c*	- 81% *d*
Ethyl dodecanoate	9,5 ± 0,0 *a*	- 53% *b*	- 65% *c*	- 81% *d*	7,5 ± 0,0 *a*	- 50% *b*	- 64% *c*	- 81% *d*	9,7 ± 0,7 *a*	- 31% *b*	- 60% *c*	- 82% *d*
Higher alcohol acetates												
Isobutyl acetate	61,2 ± 1,4	*ns*	*ns*	*ns*	66,2 ± 2,4	*ns*	*ns*	*ns*	60,1 ± 4,6	*ns*	*ns*	*ns*
Isoamyl acetate	267,9 ± 4,0	*ns*	*ns*	*ns*	274,1 ± 10,2 a	*ns*	*ns*	- 7,7% *b*	252,6 ± 20,4	*ns*	*ns*	*ns*
Propyl acetate	20,4 ± 1,6	*ns*	*ns*	*ns*	21,8 ± 0,5	*ns*	*ns*	*ns*	19,9 ± 0,9 *b*	+14% *a*	+8% *a*	+10% *a*
Butyl acetate	11,3 ± 0,1	*ns*	*ns*	*ns*	11,7 ± 0,9	*ns*	*ns*	*ns*	11,3 ± 0,2	*ns*	*ns*	*ns*
Ethyl esters branched acids												
Ethyl isobutyrate	191,2 ± 7,0	*ns*	*ns*	*ns*	201,8 ± 2,1	*ns*	*ns*	*ns*	214,8 ± 16,6	*ns*	*ns*	*ns*
Ethyl 2-methylbutanoate	23,8 ± 1,1	*ns*	*ns*	*ns*	23,5 ± 0,7	*ns*	*ns*	*ns*	27,2 ± 1,7 *a*	*ns*	- 14% *b*	- 16% *b*
Ethyl 3-methylbutanoate	38,3 ± 2,9	*ns*	*ns*	*ns*	35,6 ± 1,5	*ns*	*ns*	*ns*	39,0 ± 1,1 *a*	- 11% *b*	- 15% *bc*	- 16% *c*
Woody aroma												
trans-whiskeylactone	277,6 ± 11,7	*ns*	*ns*	*ns*	514,4 ± 25,1	*ns*	*ns*	*ns*	238,5 ± 10,4	*ns*	*ns*	*ns*
cis-whiskeylactone	350,6 ± 1,8	*ns*	*ns*	*ns*	400,8 ± 12,0	*ns*	*ns*	*ns*	462,3 ± 23,0	*ns*	*ns*	*ns*
Eugenol	11,3 ± 0,3	*ns*	*ns*	*ns*	11,6 ± 0,4	*ns*	*ns*	*ns*	10,8 ± 0,2	*ns*	*ns*	*ns*
Vanillin	1207,4 ± 33,3	*ns*	*ns*	*ns*	1353,1 ± 14,8 *a*	- 13% *b*	- 28% *b*	- 26% *b*	1269,2 ± 105,2	*ns*	*ns*	*ns*

[a] Reported as mean values ± standard deviation and expressed in µg/L wine. [b] Expressed in decline percentages during film treatment with regard to untreated wine. ns, no significant differences with regard to the untreated wine. For each individual aromatic compound, lower case letters a–d show significant differences between untreated and film-treated wines from each barrel separately ($p < 0.05$).