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María Reyes González-Centeno, Sophie Tempere, Pierre-Louis Teissedre,  
Kleopatra Chira

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1 **Use of alimentary film for selective sorption of haloanisoles from contaminated red**  
2 **wine**

3

4 María Reyes González-Centeno, Sophie Tempère, Pierre-Louis Teissedre, Kleopatra

5 Chira\*

6 Univ. Bordeaux, ISVV, EA 4577, Œnologie, 210 Chemin de Leysotte, 33140 Villenave

7 d'Ornon, France

8 INRA, ISVV, USC 1366 Œnologie, 210 Chemin de Leysotte, 33140 Villenave

9 d'Ornon, France

10 \* e-mail: [kleopatra.chira@u-bordeaux.fr](mailto:kleopatra.chira@u-bordeaux.fr)

11 **Abstract**

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

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

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

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

## 28 **1. Introduction**

29 The mouldy, musty, earthy or 'wet cardboard' off-flavours in wine commonly called « cork  
30 taint » are a serious quality-related problem for wine industry. There is no official  
31 information about the real incidence and the whole economic losses incurred worldwide by  
32 cork-tainted wine (Garde-Cerdán, Lorenzo, Zalacain, Alonso, & Salinas, 2012), but at least  
33 5% of the bottled wines are affected (Sefton & Simpson, 2005).

34 At the beginning of the eighties, the 2,4,6-trichloroanisole (TCA) was identified as the main  
35 component responsible for this flavour-damaging effect in wines (Buser, Zanier, & Tanner,  
36 1982). Although different compounds (geosmin, 1-octen-1-ol, 1-octen-3-one, 2-  
37 methylisoborneol, pyrazines, among others) have been claimed to be involved in this wine  
38 defect (Callejon, Ubeda, Rios-Reina, Morales, & Troncoso, 2016), research has been  
39 mainly focused on haloanisoles (HAs) and their corresponding precursors, halophenols  
40 (HPs). This choice is especially driven by the low detection threshold values of HAs (part-  
41 per-trillion range, ng/L), making possible their detection by consumers even under trace  
42 amounts. The occurrence of these volatile compounds in wine notably decrease its  
43 organoleptic quality, by masking the fruity notes (Tempere, Schaaper, Cuzange, de Revel,  
44 & Sicard, 2017), and compromise the consumer acceptance of the product (Prescott, Norris,  
45 Kunst, & Kim, 2005).

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

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

61 Chatonnet *et al.* (2010) revealed TCA contamination of wines that have had no contact with  
62 polluted corks, but acquired mouldy character from oak wood of new barrels used to age  
63 wine. The authors highlighted that both coopers and barrel-users seriously underestimate  
64 the problem, because the localized and random pollution of barrel staves by HAs and/or  
65 HPs makes difficult their systematic detection. According to the French Coopers  
66 Federation, the suspect cases only represent around 0.04% of barrel production and there is  
67 no significant accentuation in recent years. Meanwhile, to ensure a complete traceability to  
68 their customers, coopers increasingly control the presence of these undesirable compounds.  
69 From forest to shipping, different potential entry points of both HAs and HPs may be  
70 considered for oak wood pollution during barrel manufacture. Since the origin of HAs and  
71 HPs contamination for oak wood is not clearly identified at each individual cooperage,  
72 different strategies (yeast hulls, Fibrafix TX-R filter sheets, plastic film, milk products,  
73 grape seeds oil) are searched to eliminate or lessen the presence of these unpleasant volatile  
74 compounds in wine (Jung, Schaefer, Christmann, Hey, Fischer, & Rauhut, 2008; Mirabel,  
75 de Beauregard, Riquier, & Bertrand, 2006; Vidal, Puech, Fernández, Fauveau, Pellerin, &  
76 Vuchot, 2007). Some taste and/or aroma distorting and/or reduction effects have been noted  
77 for some of these treatments. Unfortunately, a lack of in-depth information about their  
78 impact on wine matrix and quality seems to limit significantly their widespread use in wine  
79 industry.

80 Within this context, the present research aimed i) to assess the efficacy of a plastic film  
81 (certified for alimentary uses) to remove or lessen the HAs and HPs content in polluted  
82 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.

85 **2. Materials and methods**

86 **2.1 Oak wood origin and drying conditions**

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

95 **2.2 Red wine vinification**

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

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

106 **2.3 Wine treatment and sample collection**

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

111 Wine was sampled after 8, 24 and 48h of wine-film contact, and then, bottled and stored at  
112 16 °C 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<sup>TM</sup> 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 °C for both injector and detector,  
161 and 40 °C for oven (programmed at 3 °C/min to 160 °C, and then at 5 °C/min to 220 °C, 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,

166 2,3,4,6-tetrachlorophenol; PCP, pentachlorophenol; TBP, 2,4,6-tribromophenol) were  
167 identified by comparing their retention times with those of the pure reference standards.

## 168 **2.8 Volatile composition of wines: extraction and gas chromatography analysis**

169 Woody and fruity aroma composition was determined by adapting the gas chromatography  
170 procedures described by Barbe and Bertrand (1996) and Antalick *et al.* (2010) respectively.  
171 The equipment used for woody and fruity aroma analyses consisted of an Agilent HP 5890  
172 GC (Hewlett-Packard, Wilmington, DE, USA) coupled with a mass spectrometer (Agilent  
173 HP 5972, electron impact 70 eV, eMV = 2 kV), and an Agilent HP 7890 GC (Hewlett-  
174 Packard, Wilmington, DE, USA) coupled to a quadrupole mass spectrometer (Agilent HP  
175 5975), respectively. Target compounds were identified by comparing their retention times  
176 and mass spectra with those of the pure reference standards. All samples were analyzed in  
177 duplicate. Calibration curves were established using pure reference standards analyzed  
178 under the same conditions than wine samples.

179 *Woody aroma.* For the identification of the target compounds, selected ions were  $m/z$  99 for  
180  $\beta$ -methyl- $\gamma$ -octalactone,  $m/z$  151 for vanillin,  $m/z$  164 for eugenol, and  $m/z$  83 for the  
181 internal standard (dodecan-1-ol).

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

## 187 **2.9 Sensory analysis**

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

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

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

197 *Training.* To familiarize the panelists with TCA odor, all judges were trained over a period  
198 of two weeks. Training sessions were adapted from Cravero *et al.* (2015) and consisted of  
199 tests for elucidating the individual olfactory sensitivity to TCA. First, a TCA identification  
200 test was conducted. For this purpose, various TCA (CAS number 87-40-1, grade purity of  
201 99%, Merck) solutions of the following concentrations 0, 0.1, 0.25, 0.5, 1.0, 2.0, 3.0, 4.0,  
202 8.0 and 16.0 ng/L prepared in two different matrices: distilled water and red wine (100%  
203 Merlot 2016, Languedoc Roussillon), were evaluated. The selected wine had a bag-in-box  
204 closure system to reduce the risk of cork taint. The ten TCA concentrations were presented  
205 in ascending order (from 0 to 16 ng/L), preceded by control (water or wine), which was  
206 placed in the initial position. Judges were requested to indicate if the sample was perceived  
207 to be identical or not to the control. TCA detection test was repeated in triplicate for each  
208 matrix on three consecutive days.

209 Secondly, a series of three alternative forced-choice tests (ISO-13301, 2018) with eight  
210 ascending TCA concentrations (from 0.1 to 6 ng TCA/L) were carried out in red wine  
211 (100% Merlot 2016, Languedoc Roussillon). For each TCA concentration, three glasses  
212 were proposed: two controls and a third one containing the substance under test. Sensory  
213 panel was asked to identify the odd sample olfactory perceived as different from the others.  
214 This sensory test was repeated in triplicate on three consecutive days. Best Estimate  
215 Threshold (BET)-method was used to calculate the TCA threshold of the sensory panel.  
216 The individual BET was calculated as the geometric mean of the highest concentration  
217 missed and the next higher concentration (the lowest TCA concentration detected within a  
218 series of correct answers). The sensory panel BET was determined as the geometric mean  
219 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<sup>2</sup> 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**

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

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

## 288 3. Results and discussion

### 289 3.1 Haloanisoles and halophenols content of wines

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

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

308 HAs have very low detection thresholds in alcoholic solution (in the range of ng/L), which  
309 make their mouldy, musty, earthy or 'wet cardboard' off-flavours easily recognizable  
310 (Callejón, Ubeda, Ríos-Reina, Morales, & Troncoso, 2016). In the case of TCA, published  
311 detection threshold may vary considerably depending not only on panel expertise,  
312 sensitivity and training, but also on wine style and matrix (Mazzoleni & Maggi, 2007).  
313 Specifically, the most extended values of TCA perception threshold in red wine range  
314 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  $65 \pm 1$  and malic,



342 lactic and tartaric acid contents of 0.4, 0.8 and 2.2 g/L wine, respectively. Thus, the use of  
343 the plastic film to eliminate/reduce both HA and HP content in wines did not influence their  
344 oenological parameters, and this regardless of the contact time of the film-treatment.  
345 Chromatic characteristics (color intensity, hue and yellow, red and blue components) of all  
346 wines analyzed are depicted in Figure 1. A priori, no chromatic parameter really changed  
347 because of the film treatment and/or the contact time film-wine. Nevertheless, some  
348 differences between untreated and film-treated wines, and even among wines treated with  
349 film for different contact times, were found to be statistically significant ( $p < 0.05$ ). These  
350 differences ( $\leq 6\%$  with regard to the corresponding untreated wine) were mainly attributed  
351 to the highly reproducibility of the absorbance measurements, but they were not visually  
352 perceived by any taster during sensory analysis.

### 353 **3.3 Total phenolic, proanthocyanidin and anthocyanin content**

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

360 With regard to the anthocyanin results, film-treated wines from barrels A and C displayed a  
361 little but significant rise of total anthocyanins at 48h and 24h of contact, respectively ( $p <$   
362  $0.05$ ). This increase suggested that the plastic film might absorb certain wine components  
363 that anthocyanins are used to combine. In fact, anthocyanins are the main pigments present  
364 in young red wines, being responsible for their intense red color. During oak wood wine  
365 aging anthocyanins can yield polymeric pigments by their reaction with flavanols (directly  
366 or mediated by aldehydes). Moreover, A-type vitisins (the main pyranoanthocyanins found  
367 in red wines) can also react with other wine components giving origin to polymeric  
368 pigments with different colors ranging from yellow to turquoise blue.

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

### 372 **3.4 Anthocyanin composition of wines**

373 Since some evolution of the total anthocyanin content was observed during the film  
374 treatment, the anthocyanin profile of both untreated and film-treated wines was also  
375 analyzed to get in-depth information. The total anthocyanin content of all wines, calculated  
376 by adding up the individual concentration of each anthocyanin compound, ranged from  
377 38.5 to 45.1 mg Mlv/L wine. The same anthocyanin profile was observed for both untreated  
378 and film-treated wines, malvidin-3*O*-glucoside being the most abundant component and  
379 accounting for 29–32% of the total anthocyanin fraction. In all cases, delphinidin-3*O*-  
380 glucoside was the second main anthocyanin (~15%), followed by similar concentrations of  
381 both petunidin and peonidin (~13%), and then, the acetyl form of malvidin (~11%),  
382 cyanidin (~9%) and the acetyl form of peonidin (~8%), in that order (Table 3).

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

### 391 **3.5 Volatile composition of wines**

#### 392 *3.5.1 Woody aroma*

393 The evolution of the main direct contributors to the overall woody aroma (whiskeylactones,  
394 eugenol, vanillin) during film-treatment is also described in Table 4. Woody aroma profile  
395 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  $\geq 31\%$  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, &

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

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

### 437 **3.6 Sensory analysis**

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

442 *Wine evaluation.* According to the results of the triangle test, sensory panel significantly  
443 distinguished between untreated wines and film-treated wines after 8h, 24h and 48h of film  
444 contact for barrels A (52% of correct answers,  $p \leq 0.007$ ), C (50% of correct answers,  $p \leq$   
445 0.016) and B (50% of correct answers,  $p \leq 0.016$ ), respectively. Specifically, these film-  
446 treatments corresponded to a reduction of TCA pollution under the limit of quantification  
447 (0.5 ng/L) in the case of barrel A, and a decrease of 75% and 83% of the initial TCA  
448 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.

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

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

### 496 **3.7 Impact of the film treatment on flavan-3-ol composition and fruity character of** 497 **wines**

498 *Flavan-3-ol composition of wines.* As previously described in section 3.3, total  
499 proanthocyanidin content of film-treated wines did not change significantly compared to  
500 untreated wine. The analysis of the flavan-3-ol profile performed in the additional  
501 experiment corroborated those results, since regardless of the TCA supplementation level  
502 applied, all film-treated wines presented the same flavan-3-ol content and profile than  
503 control wine. As observed in Table S2 (at the Supplementary material section), neither  
504 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.

531 **4. Conclusions**

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

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

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## 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**

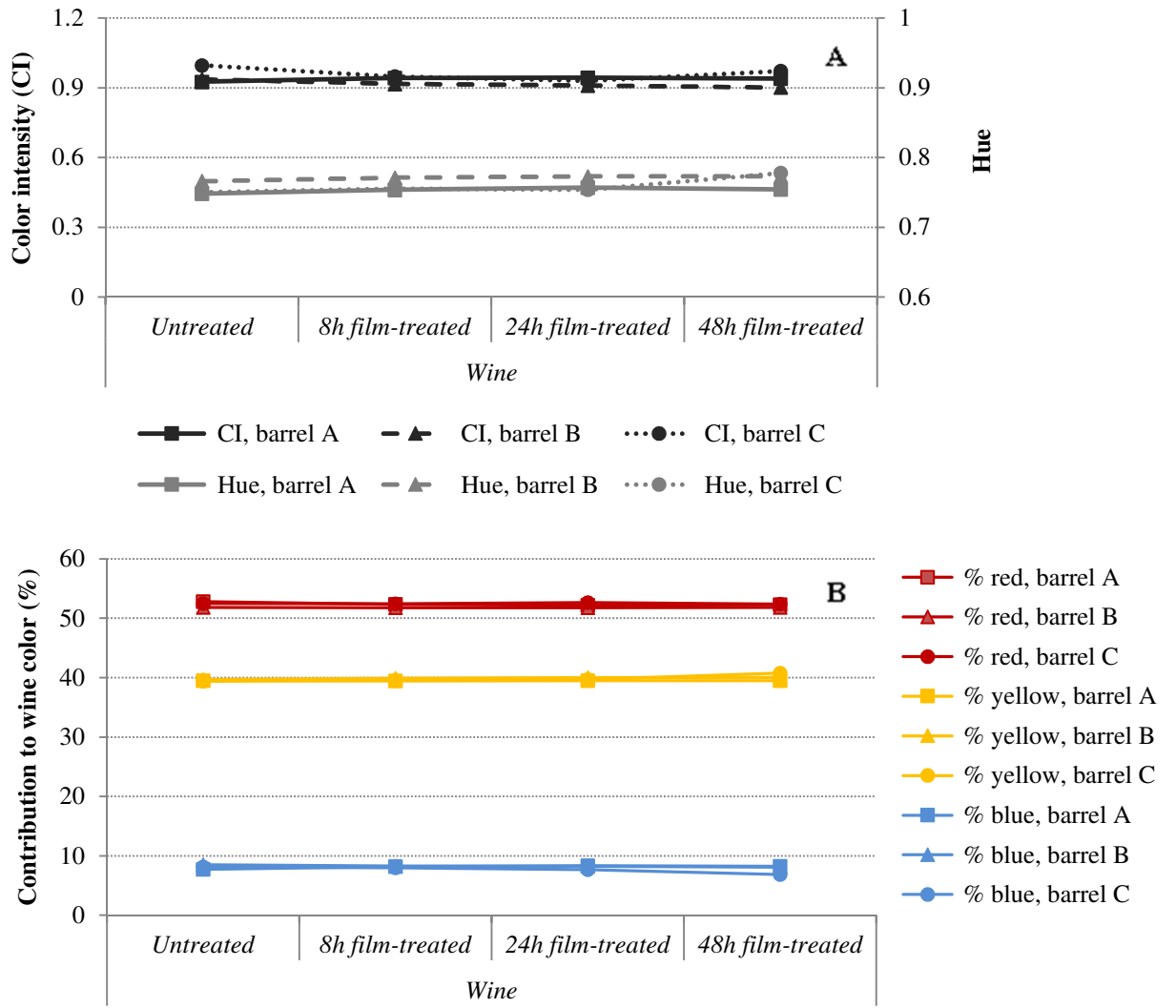
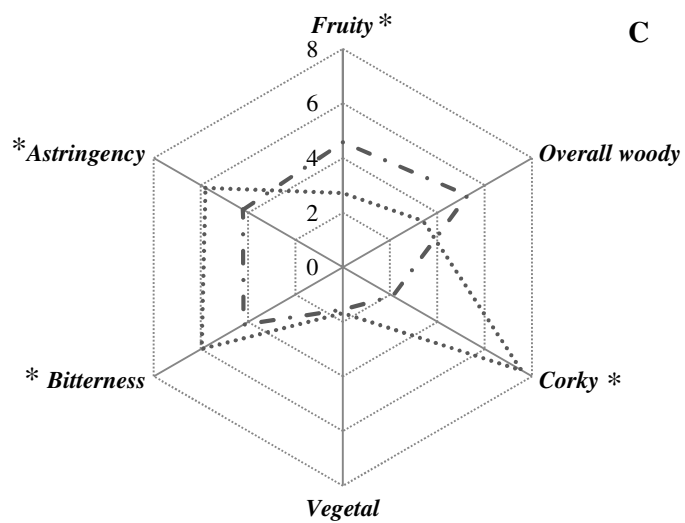
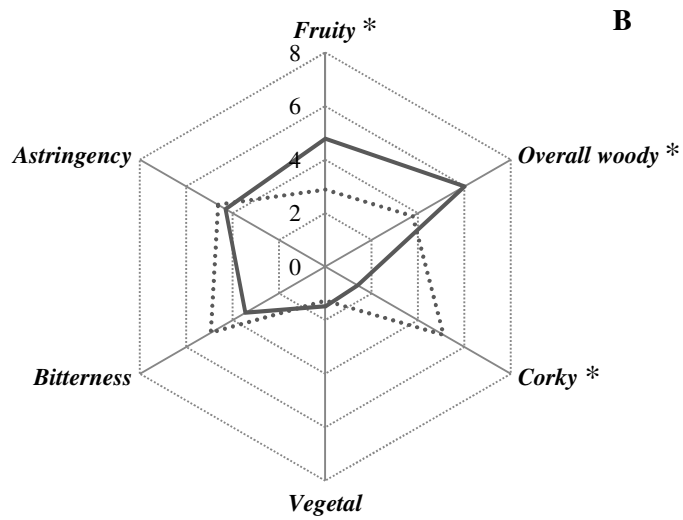
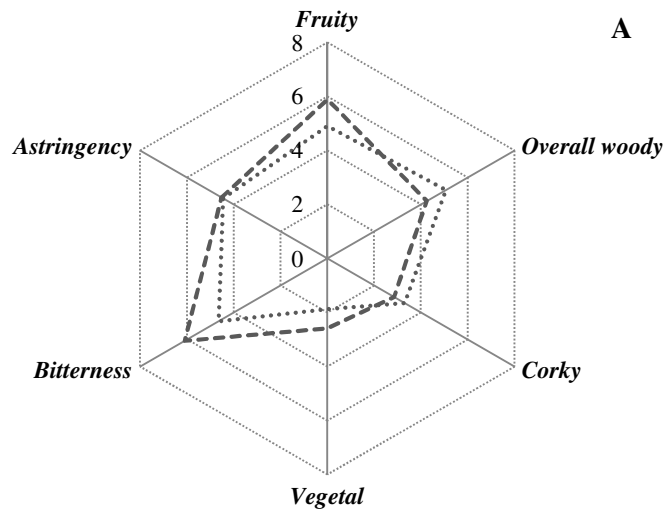


Figure 2



..... 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
<b>Barrel A</b>								
<i>Untreated wine</i>	1,0	< LoQ	< LoQ	nd	8,1	< LoQ	3,9	< LoQ
<i>8h film-treated wine</i>	< LoQ	< LoQ	< LoQ	nd	8,6	< LoQ	3,1	< LoQ
<i>24h film-treated wine</i>	< LoQ	< LoQ	< LoQ	nd	5,6	< LoQ	3,1	nd
<i>48h film-treated wine</i>	nd	< LoQ	< LoQ	nd	5,4	< LoQ	< LoQ	nd
<b>Barrel B</b>								
<i>Untreated wine</i>	3,0	< LoQ	nd	nd	11,8	< LoQ	5,3	< LoQ
<i>8h film-treated wine</i>	1,6	nd	nd	nd	12,3	< LoQ	< LoQ	< LoQ
<i>24h film-treated wine</i>	0,8	nd	nd	nd	13,8	< LoQ	< LoQ	< LoQ
<i>48h film-treated wine</i>	0,5	nd	nd	nd	11,1	< LoQ	< LoQ	nd
<b>Barrel C</b>								
<i>Untreated wine</i>	9,1	< LoQ	nd	nd	64,3	< LoQ	< LoQ	< LoQ
<i>8h film-treated wine</i>	3,9	nd	nd	nd	59,7	< LoQ	< LoQ	< LoQ
<i>24h film-treated wine</i>	2,3	nd	nd	nd	63,9	< LoQ	< LoQ	< LoQ
<i>48h film-treated wine</i>	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 <sup>a</sup>	Total proanthocyanidins <sup>b</sup>	Total anthocyanins <sup>c</sup>
<b>Barrel A</b>			
<i>Untreated wine</i>	2891 ± 36 <i>a</i>	3,5 ± 0,2 <i>b</i>	133,4 ± 4,0 <i>b</i>
<i>8h film-treated wine</i>	2876 ± 45 <i>a</i>	3,7 ± 0,1 <i>b</i>	138,8 ± 4,6 <i>ab</i>
<i>24h film-treated wine</i>	2874 ± 87 <i>a</i>	4,1 ± 0,1 <i>a</i>	147,0 ± 3,4 <i>ab</i>
<i>48h film-treated wine</i>	2766 ± 36 <i>b</i>	3,6 ± 0,1 <i>b</i>	149,5 ± 9,3 <i>a</i>
<b>Barrel B</b>			
<i>Untreated wine</i>	2781 ± 77 <i>a</i>	3,7 ± 0,2 <i>a</i>	171,9 ± 3,4 <i>a</i>
<i>8h film-treated wine</i>	2782 ± 125 <i>a</i>	4,1 ± 0,2 <i>a</i>	177,2 ± 5,6 <i>a</i>
<i>24h film-treated wine</i>	2750 ± 68 <i>a</i>	3,8 ± 0,3 <i>a</i>	175,1 ± 7,6 <i>a</i>
<i>48h film-treated wine</i>	2852 ± 57 <i>a</i>	3,6 ± 0,6 <i>a</i>	165,1 ± 2,2 <i>a</i>
<b>Barrel C</b>			
<i>Untreated wine</i>	2847 ± 134 <i>a</i>	3,7 ± 0,2 <i>a</i>	144,9 ± 10,2 <i>b</i>
<i>8h film-treated wine</i>	2814 ± 122 <i>a</i>	3,5 ± 0,3 <i>a</i>	160,2 ± 7,2 <i>ab</i>
<i>24h film-treated wine</i>	2809 ± 117 <i>a</i>	3,6 ± 0,1 <i>a</i>	171,1 ± 5,5 <i>a</i>
<i>48h film-treated wine</i>	2852 ± 67 <i>a</i>	3,6 ± 0,2 <i>a</i>	169,6 ± 3,8 <i>a</i>

All results are reported as mean values ± standard deviation. <sup>a</sup>Total phenolics expressed as mg gallic acid/L wine. <sup>b</sup>Total proanthocyanidins expressed as g tannins/L wine. <sup>c</sup>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
<i>Dp-3O-glc</i>	5,8 ± 0,1 <i>b</i>	6,0 ± 0,1 <i>a</i>	6,1 ± 0,0 <i>a</i>	6,1 ± 0,0 <i>a</i>	6,5 ± 0,1 <i>a</i>	6,7 ± 0,2 <i>a</i>	6,7 ± 0,0 <i>a</i>	6,7 ± 0,0 <i>a</i>	5,6 ± 0,1 <i>c</i>	6,1 ± 0,0 <i>b</i>	6,3 ± 0,0 <i>a</i>	6,2 ± 0,0 <i>a</i>
<i>Cy-3O-glc</i>	3,7 ± 0,0 <i>b</i>	3,8 ± 0,0 <i>a</i>	3,8 ± 0,0 <i>a</i>	3,8 ± 0,0 <i>a</i>	3,8 ± 0,1 <i>a</i>	3,9 ± 0,0 <i>a</i>	3,9 ± 0,0 <i>a</i>	3,9 ± 0,0 <i>a</i>	3,7 ± 0,0 <i>a</i>	3,8 ± 0,0 <i>a</i>	3,8 ± 0,0 <i>a</i>	3,8 ± 0,0 <i>a</i>
<i>Pt-3O-glc</i>	5,4 ± 0,0 <i>a</i>	5,4 ± 0,0 <i>a</i>	5,4 ± 0,1 <i>a</i>	5,4 ± 0,0 <i>a</i>	5,7 ± 0,0 <i>a</i>	5,9 ± 0,1 <i>a</i>	5,9 ± 0,1 <i>a</i>	5,9 ± 0,2 <i>a</i>	5,1 ± 0,0 <i>b</i>	5,5 ± 0,0 <i>a</i>	5,4 ± 0,0 <i>a</i>	5,5 ± 0,1 <i>a</i>
<i>Pn-3O-glc</i>	5,3 ± 0,1 <i>a</i>	5,5 ± 0,0 <i>a</i>	5,4 ± 0,2 <i>a</i>	5,4 ± 0,1 <i>a</i>	5,6 ± 0,1 <i>a</i>	5,7 ± 0,1 <i>a</i>	5,7 ± 0,1 <i>a</i>	5,8 ± 0,0 <i>a</i>	5,2 ± 0,1 <i>b</i>	5,5 ± 0,0 <i>a</i>	5,5 ± 0,0 <i>a</i>	5,5 ± 0,0 <i>a</i>
<i>Mlv-3O-glc</i>	11,8 ± 0,1 <i>b</i>	12,7 ± 0,3 <i>a</i>	12,8 ± 0,1 <i>a</i>	12,6 ± 0,1 <i>a</i>	13,7 ± 0,1 <i>b</i>	14,5 ± 0,0 <i>a</i>	14,4 ± 0,1 <i>a</i>	14,4 ± 0,2 <i>a</i>	11, <sub>3</sub> ± 0,1 <i>c</i>	12, <sub>8</sub> ± 0,0 <i>b</i>	13, <sub>1</sub> ± 0,0 <i>a</i>	12, <sub>9</sub> ± 0,1 <i>b</i>
<i>Pn-3O-acglc</i>	3,4 ± 0,0 <i>a</i>	3,5 ± 0,0 <i>a</i>	3,4 ± 0,0 <i>a</i>	3,4 ± 0,0 <i>a</i>	3,5 ± 0,0 <i>a</i>	3,5 ± 0,0 <i>a</i>	3,5 ± 0,0 <i>a</i>	3,5 ± 0,0 <i>a</i>	3,4 ± 0,0 <i>b</i>	3,5 ± 0,0 <i>a</i>	3,5 ± 0,0 <i>a</i>	3,4 ± 0,0 <i>ab</i>
<i>Mlv-3O-acglc</i>	4,4 ± 0,0 <i>a</i>	4,4 ± 0,1 <i>a</i>	4,4 ± 0,0 <i>a</i>	4,4 ± 0,0 <i>a</i>	4,7 ± 0,0 <i>b</i>	4,8 ± 0,1 <i>ab</i>	4,8 ± 0,1 <i>ab</i>	4,9 ± 0,0 <i>a</i>	4,3 ± 0,1 <i>b</i>	4,4 ± 0,0 <i>ab</i>	4,4 ± 0,1 <i>ab</i>	4,5 ± 0,0 <i>a</i>

All results are reported as mean values ± standard deviation and expressed in mg malvidin/L wine. *Glc*, monoglucoside; *acglc*, 6"-acetylglucoside; *Dp*, delphinidin; *Cy*, cyaniding; *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 <sup>a</sup>	8h film-treated wine <sup>b</sup>	24h film-treated wine <sup>b</sup>	48h film-treated wine <sup>b</sup>	Untreated wine <sup>a</sup>	8h film-treated wine <sup>b</sup>	24h film-treated wine <sup>b</sup>	48h film-treated wine <sup>b</sup>	Untreated wine <sup>a</sup>	8h film-treated wine <sup>b</sup>	24h film-treated wine <sup>b</sup>	48h film-treated wine <sup>b</sup>
<b>Fruity aroma</b>												
<i>Ethyl esters of straight-chain fatty acids</i>												
<i>Ethyl propanoate</i>	262,4 ± 15,2	ns	ns	ns	297,0 ± 15,2	ns	ns	ns	283,0 ± 18,5	ns	ns	ns
<i>Ethyl butanoate</i>	123,8 ± 3,6	ns	ns	ns	132,4 ± 8,1	ns	ns	ns	129,3 ± 9,3	ns	ns	ns
<i>Ethyl hexanoate</i>	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
<i>Ethyl octanoate</i>	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
<i>Ethyl decanoate</i>	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
<i>Ethyl dodecanoate</i>	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
<i>Higher alcohol acetates</i>												
<i>Isobutyl acetate</i>	61,2 ± 1,4	ns	ns	ns	66,2 ± 2,4	ns	ns	ns	60,1 ± 4,6	ns	ns	ns
<i>Isoamyl acetate</i>	267,9 ± 4,0	ns	ns	ns	274,1 ± 10,2 a	ns	ns	- 7,7% b	252,6 ± 20,4	ns	ns	ns
<i>Propyl acetate</i>	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
<i>Butyl acetate</i>	11,3 ± 0,1	ns	ns	ns	11,7 ± 0,9	ns	ns	ns	11,3 ± 0,2	ns	ns	ns
<i>Ethyl esters branched acids</i>												
<i>Ethyl isobutyrate</i>	191,2 ± 7,0	ns	ns	ns	201,8 ± 2,1	ns	ns	ns	214,8 ± 16,6	ns	ns	ns
<i>Ethyl 2-methylbutanoate</i>	23,8 ± 1,1	ns	ns	ns	23,5 ± 0,7	ns	ns	ns	27,2 ± 1,7 a	ns	- 14% b	- 16% b
<i>Ethyl 3-methylbutanoate</i>	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
<b>Woody aroma</b>												
<i>trans-whiskeylactone</i>	277,6 ± 11,7	ns	ns	ns	514,4 ± 25,1	ns	ns	ns	238,5 ± 10,4	ns	ns	ns
<i>cis-whiskeylactone</i>	350,6 ± 1,8	ns	ns	ns	400,8 ± 12,0	ns	ns	ns	462,3 ± 23,0	ns	ns	ns
<i>Eugenol</i>	11,3 ± 0,3	ns	ns	ns	11,6 ± 0,4	ns	ns	ns	10,8 ± 0,2	ns	ns	ns
<i>Vanillin</i>	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

<sup>a</sup> Reported as mean values ± standard deviation and expressed in µg/L wine. <sup>b</sup> 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 ( $p < 0.05$ ).