

1 **Sensory and chemical drivers of wine minerality aroma: An application to Chablis wines**

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15

16 **Abstract**

17 The goal of this work was to evaluate the effect of vineyard position on the minerality of  
18 wines and to establish relationships between minerality scores, sensory descriptors and  
19 chemical composition. Sensory analyses included minerality rating and free description  
20 performed by wine professionals under two conditions: orthonasal olfaction alone and global  
21 tasting. Chemical characterization included analysis of major and minor volatile compounds,  
22 volatile sulphur compounds, mercaptans, metals, anions and cations. Results showed a  
23 significant effect of the river bank on wine minerality scores only in the orthonasal olfaction  
24 condition, samples from the left being more mineral than those from the right bank.  
25 Methanethiol, involved in shellfish aroma, was significantly higher in wines from the left  
26 (more mineral) than from the right bank. Contrary, copper levels, related to lower levels of  
27 free MeSH, and norisoprenoids, responsible for white fruit and floral aromas, were higher in  
28 wines from the right bank (less mineral).

29 **Keywords:** minerality; Chablis; Chardonnay; methanethiol; river bank; shellfish aroma

## 30 1. Introduction

31 Flavour plays an important role in food and beverages appreciation and consumption. Flavour  
32 perception is a system that involves diverse chemical compounds, peripheral receptors and the  
33 brain, resulting in a very complex system. An example of this complexity is wine, an  
34 alcoholic beverage comprising a wide range of volatile and non-volatile components  
35 interacting to form wine flavour. Quantification of sensory-active molecules has been useful  
36 for instance in better understanding the perceived quality of wines of different varieties and  
37 regions (Saénz-Navajas et al., 2015), understanding the source of some wine aroma  
38 descriptors (Ferreira, Sáenz-Navajas, Campo, Herrero, de la Fuente & Fernandez-Zurbano,  
39 2016) and disclosing wine styles (Liu et al., 2015). One of the most intriguing wine styles is  
40 mineral wines. Minerality is an ill-defined sensory descriptor widely used nowadays, though  
41 absent from the famous “Wine Aroma Wheel” (Noble, Arnold, Masuda, Pecore, Schmidt &  
42 Stern., 1984).

43 Recently, this term has been popularized by critics, winemakers and consumers, and has  
44 caught researchers’ attention. As a result, a number of studies have been conducted to better  
45 understand this ill-defined sensory descriptor. Most of these studies were rather descriptive.  
46 Some focused on sensory perception, through the relationship between minerality and  
47 sensory descriptors like reductive notes, sulphur, cabbage, cardboard, flinty/smoky,  
48 chalky/calcareous, wet stone, citrus, and fresh, which are positively correlated with the  
49 mineral character and tropical fruits, passion fruit, butter, butterscotch, vanilla and oak which  
50 are negatively correlated with this character (Ballester, Mihnea, Peyron & Valentin, 2013;  
51 Parr, Ballester, Peyron, Grose & Valentin, 2015; Heymann, Hopfer & Bershaw, 2014). Other  
52 studies were based on the correlation between sensory perception of minerality and chemical  
53 composition of the wines. According to Heymann, Hopfer & Bershaw, (2014), perceived  
54 minerality was moderately associated with free and total sulphur dioxide and strongly

55 associated with malic acid, TA and tartrate level which supported the idea that sour taste  
56 would be involved in wine minerality. Moreover, in the particular case of Sauvignon blanc  
57 (Parr et al. 2016), the significant associations differed as a function of participant culture: for  
58 French assessors, minerality was positively associated with isoamyl acetate and free sulphur  
59 dioxide while other compounds as total acidity and tartaric acid, were negatively associated .  
60 For New Zealanders assessors, minerality was positively correlated with Na, Ca, total sulphur  
61 dioxide, malic acid and hexanoic acid and was negatively correlated with isoamyl alcohol,  
62 isobutanol and diethyl succinate.

63 Only a few studies looked at the theoretical origin of minerality. Baroň & Fiala (2012)  
64 hypothesized that minerality could come from yeast metabolism during the fermentation of  
65 musts poor in nitrogen. From a geological perspective, according to Maltman (2013) the  
66 minerals in wine are nutrient elements (typically metallic cations) and are only distantly  
67 related to vineyard geological minerals, which are complex crystalline compounds. Finally,  
68 Rodrigues, Ballester, Saenz-Navajas & Valentin (2015) and Deneulin & Bavaud (2016)  
69 looked at the conceptual aspects of perceived minerality and highlighted the idea of “*terroir*”  
70 as the origin of minerality in the mind of consumers. However despite these scientific efforts,  
71 the origin of minerality remains unclear.

72 The general goal of the present study is to verify if the idea of an origin of the minerality in  
73 the *terroir* has a scientific foundation. According to Van Leeuwen and Seguin (2006), *terroir*  
74 is “*concerned with the relationship between the characteristics of an agricultural product*  
75 *(quality, taste, style) and its geographic origin, which might influence these characteristics*”.

76 As it is very difficult to assess the joint effect of all the different geographic variables (soils,  
77 climate, microclimate, slope, etc) that make up a *terroir* (Van Leeuwen. Friant, Chone,  
78 Tregoeat, Koundouras & Dubourdieu, 2004) the effects caused by those parameters on vine,  
79 grapes or wine have been independently reported (Van Leeuwen and Seguin, 1994).

80 According to Bramley and Hamilton (2007), vineyards are not homogeneous and different  
81 wine styles can emerge from different parts of the same vineyard even when similar  
82 agricultural management is implemented. Within-vineyard variability can be attributed to  
83 either climate variability (i.e. what van Leeuwen & Seguin, 2006 called meso climatic  
84 variability) or soil variations (i.e. what van Leeuwen & Seguin, 2006 called topoclimatic  
85 variability). This is particularly the case of terroirs characterized by complex morphology as  
86 slopes and elevations. In this sense, different authors contemplate the study of vineyards  
87 variability from: a Precision Agriculture (PA) viewpoint (Bramley, 2001), from a grape berry  
88 quality perspective (Fourment, Ferrer, González-Neves, Barbeau, Bonnardot & Quenol, 2013)  
89 and considering the effects of topoclimatic variability on final wines (Bramley & Hamilton,  
90 2007). This last approach is one of the few which demonstrated clear differences among  
91 sensory attributes of wines produced from areas of lower and higher grape yield and vine  
92 vigor within the same vineyards under uniform management.

93 In France, vineyard variability lead to the notion of *Crus* and an example of this is the AOC  
94 “Chablis *Premier Cru*”. Depending on the specific geographic origin of grapes and thus on  
95 “topoclimatic variability” wines coming from a given cru can be fruitier or conversely more  
96 mineral than wines coming from another cru (Cahier des Charges de l’Appellation Chablis,  
97 2011). The present work focuses on Chablis Premier Cru AOC: **This AOC is marked by a  
98 temperate oceanic climate with continental trends (see agroclimatic data of Chablis zone in  
99 supplementary material 1) and** has the peculiarity of being planted along both banks (right and  
100 left) of the Serein river (Figure 1). According to Cannard (1999) the right bank has vineyards  
101 with predominant southwest sun exposure that can facilitate the grape maturity and the wines  
102 tend to be fruitier. On the other hand, the left bank tend to have southeast sun exposure, and  
103 thus less is conducive to maturation.

104 Building on this topoclimatic variability, to evaluate the effect of terroir on wine minerality  
105 we looked at the effect of the Serein river bank on perceived minerality intensity of Chablis  
106 wines and we identified the sensory and chemical drivers of this effect. More specifically, the  
107 following two questions were addressed: 1) which river bank produces the more mineral  
108 wines? 2) Which are the sensory and chemical compounds associated with perceived mineral  
109 intensity?

## 110 **2. Materials and Methods**

### 111 *2.1. Sensory and chemical characterization of wines*

#### 112 *2.1.1. Wines*

113 Eight wines were selected among the AOC Chablis Premier Cru: four originating from the left  
114 bank of Serein (*Cote de Léchet, Montmains, Vaillons and Beauroy*) and four from the right  
115 bank (*Montée de Tonnerre, Mont de Milieu, Fourchaume and Vaucoupin*). **To avoid an**  
116 **interaction between minerality and vintage** all wines were from the 2013 vintage. **Likewise to**  
117 **avoid other confounds like aging and vinification process** all wines were aged one year in  
118 **bottle and were elaborated by the same wine producer using the same winemaking process in**  
119 **stainless steel tanks**. The list of samples, including sample information and basic  
120 compositional data is shown in Table 1.

#### 121 *2.1.2. Sensory analysis*

##### 122 *2.1.2.1. Assessors*

123 Thirty two wine professionals (69% men and 31% women, aged between 23 and 61 years old,  
124 average = 42 years) participated in this study. **They were not informed of the topic of the**  
125 **study**. All of them were wine producers from the Chablis area.

##### 126 *2.1.2.2. Experimental conditions*

127 Assessors were first asked to read and sign a consent form. Wines were presented at room  
128 temperature, in black ISO glasses identified only by random three-digit codes. The poured  
129 volume per sample was 25 mL. Samples were presented according to a Williams Latin Square  
130 arrangement. Evian water and unsalted crackers were available for palate rinsing. Participants  
131 were asked not to swallow the samples but to expectorate into wine spittoons. The sessions  
132 were performed in two different days and the average duration of each session was 40 min. In  
133 both the first and second sessions, participants were invited to evaluate the perceived  
134 minerality intensity of the samples. In the second session, participants were additionally asked  
135 to carry out a free description of the samples after having rated their minerality.

#### 136 *2.1.2.3. Minerality rating*

137 During the first session, assessors were presented with the eight wines and asked to smell  
138 each sample from left to right and to score their minerality on a seven-point scale, from 1  
139 (absent) to 7 (very intense) based on orthonasal olfaction alone. **Assessors were free to**  
140 **compare them before scoring if they wanted.** Then, they were asked to taste each wine and to  
141 score their minerality on the same seven-point scale based on global tasting. This minerality  
142 rating procedure was replicated in the second session, with the same wines presented with  
143 different codes.

#### 144 *2.1.2.4. Free description task*

145 In the second session, after completion of the minerality rating task, eight new glasses of wine  
146 with the same samples but with different codes were served. Participants were asked to  
147 describe sample aroma by orthonasal olfaction alone first and then by global tasting (aroma  
148 and in-mouth properties).

#### 149 *2.1.3. Chemical analysis*

##### 150 *2.1.3.1. Reagents and standards*

151 *Solvents.* N-hexane for organic trace analysis (UniSolv), dichloromethane and methanol of  
152 SupraSolv quality and ethanol of LiChrosolv quality were purchased from Merck (Darmstadt,  
153 Germany). Diethyl ether and mercaptoglycerol were from Merck (Darmstadt, Germany). Water  
154 was purified in a Milli-Q system from Millipore (Bedford, MA).

155 *Resins.* SPE cartridges were supplied by Merck (Darmstadt, Germany).

156 *Standards.* The chemical standards were supplied by Sigma (St. Louis, MO), Aldrich  
157 (Gillingham, U.K.), Fluka (Buchs, Switzerland), Lancaster (Strasbourg, France), PolyScience  
158 (Niles, IL), Chem Service (West Chester, PA), Merck (Darmstadt, Germany), Panreac  
159 (Barcelona, Spain), Oxford Chemicals (Hatlepool, UK), Alfa Aesar (Ward Hill, MA) and  
160 Firmenich (Geneva, Switzerland), as indicated in Table 2. Ethyl heptanoate, heptanoic acid, 4-  
161 hydroxy-4-methyl-2-pentanone, 3-octanone, 2-octanol, 3,4-dimethylphenol, 1,8-  
162 diazabicyclo[5.4.0]undec-7-ene (DBU) and octafluoronaftalene were purchased from Aldrich,  
163 2-octanol and 4-methyl-2-pentanol from PolyScience and 2-butanol from Panreac (Barcelon,  
164 Spain) and 2-phenylethanethiol and *O*-methylhydroxylamine hydrochloride from Fluka.  
165 Purity of chemical standards was over 95% in all cases, and most of them over 99%.

166 *Reagents.* Sodium chloride, L-tartaric acid, ammonium sulphate, and NaHCO<sub>3</sub> were supplied  
167 by Panreac (Barcelona, Spain). L-cystein hydrochloride hydrate 99% and  
168 ethylenediaminetetracetic disodium salt 2-hydrate (EDTA) were purchased from Aldrich  
169 (Steinheim, Germany).

#### 170 *2.1.3.2. Conventional oenological parameter determination*

171 Ethanol content, pH, reducing sugars, titratable (total) and volatile acidities were determined  
172 by Infrared Spectrometry with Fourier Transformation (IRFT) with a WineScan<sup>TM</sup> FT 120  
173 (FOSS<sup>®</sup>), which was calibrated with wine samples analysed in accordance with official OIV  
174 (International Organization of Vine and Wine) practices. Malic and lactic acids were  
175 determined by enzymatic methods using an enzymatic autoanalyser (LISA 200 Wine



176 Analyzer System). Total and free sulphur dioxide were determined by the aspiration/titration  
177 method (Rankine method) recommended by the OIV. All conventional analyses were  
178 performed in duplicate.

### 179 2.1.3.3. Volatile composition analysis

180 Major compounds were isolated by liquid-liquid extraction and analysed in a gas  
181 chromatograph with flame ionization detector (GC-FID) following the method described by  
182 Ortega, Lopez, Cacho and Ferreira (2001) but with some modifications. Accordingly, wine  
183 samples (2.7 mL) were adjusted to 12% (v/v) of alcohol and demixed by the addition of  
184 ammonium sulphate (4.05 g). Then, 20  $\mu\text{L}$  of an internal standard solution was added  
185 (concentration of 150  $\text{mg L}^{-1}$  of ethyl heptanoate, heptanoic acid, 4-hydroxy-4-methyl-2-  
186 pentanone, 2-octanol, 2-butanol and 4-methyl-2-pentanol) followed by 250 mL of  
187 dichloromethane. The mixture was stirred during 90 min at 90 rpm. The organic extract was  
188 analysed by GC-FID with a Varian GC-3800 gas chromatograph. The column (30 m x 0.32  
189 mm x 0.5  $\mu\text{m}$ ) was a DB-WAX from J & W Scientific (Folsom, CA, USA). The column was  
190 preceded by a 3m x 0.32 mm uncoated precolumn from Agilent Technologies (Santa Clara,  
191 CA, USA). The temperature program was as follows: 40°C for 5 min, raised at 4°C  $\text{min}^{-1}$  up to  
192 102°C, then raised at 4°C  $\text{min}^{-1}$  up to 112°C and raised again at 3°C  $\text{min}^{-1}$  up to 125°C and  
193 kept at this temperature during 5 min. Then, raised at 3°C  $\text{min}^{-1}$  up to 160°C and raised again  
194 at 6°C  $\text{min}^{-1}$  up to 200°C. Finally, it was kept at 200°C during 30 min. Carrier gas was He at  
195 2.2  $\text{mL min}^{-1}$ . Injection: 2  $\mu\text{L}$  in split mode (1:20) and temperature of injector and detector:  
196 250°C. Analytes were referred to a selected internal standard and response factor was the  
197 selected method for calibration.

198 Minor and trace compounds were isolated through solid-phase extraction (SPE) and analysed  
199 by gas chromatography coupled to a mass spectrometry detection system (GC-MS), as

200 explained by Lopez, Aznar, Cacho and Ferreira (2002). Accordingly, 15 mL of wine were  
201 submitted to solid-phase extraction (SPE) using an extraction unit (VAC ELUT 20 Station  
202 from Varian). SPE cartridges filled with 65 mg of LICHrolut EN resins were firstly  
203 conditioned with 2 mL of dichloromethane, 2 mL of methanol and 2 mL of a hydroalcoholic  
204 solution (12% v/v). After this, 15 mL of wine (containing a solution of internal standards: 3-  
205 octanone, 2-octanol, 3,4-dimethylphenol at 75 mg L<sup>-1</sup>) were loaded. Then, the cartridge was  
206 washed with 1.5 mL of an aqueous solution (containing 30% methanol and 1% of NaHCO<sub>3</sub>).  
207 Finally, once the cartridge was dry, aroma compounds were eluted with 0.6 mL of  
208 dichloromethane containing 5% of methanol (v/v). This extract was analysed by GC-MS  
209 using a Varian GC-450 (Walnut Creek, CA, USA) gas chromatograph coupled to a Saturn  
210 2200 ion-trap detector. The column was a DB-WAX ETR from Agilent- J & W Scientific  
211 (Folsom, CA, USA), 60 m x 0.25 mm with 0.25 µm i.d. and preceded by a 3m x 0.25 mm  
212 deactivated uncoated precolumn. The carrier was He at 1.5 mL min<sup>-1</sup>. Injection conditions  
213 were as follows: at 55 °C during 0.40 min and then raised at 200°C min<sup>-1</sup> up to 300°C. Two µL  
214 of sample were injected in splitless mode. The temperature program was as follows: 40°C for  
215 3 min, raised at 2°C min<sup>-1</sup> up to 220°C, and finally kept at this temperature during 60 min.  
216 Spectra were acquired in 35-220 *m/z* range in SCAN mode. Analytes were referred to a  
217 selected internal standard and response factor was the selected method for calibration.

218 Quantitative analysis of polyfunctional mercaptans was carried out using the method proposed  
219 by Mateo-Vivaracho, Cacho and Ferreira (2008). Therefore, a first SPE derivatization with  
220 2,3,4,5,6-pentafluorobenzylbromide (PFBBBr) was carried out and analysed in a GC-MS  
221 system with negative chemical ionization (NCI). Accordingly, in a 20-mL flask, 10 mL of  
222 wine were spiked with 0.05 g of EDTA, 0.156 g of L-cystein and a solution of internal  
223 standard (1400 µg L<sup>-1</sup> of 2-phenylethanethiol). This solution was transferred to a vial and 0.2

224 g of *O*-methylhydroxylamine were added and heated up to 55°C during 45min. Six millilitres  
225 of this sample were loaded onto a 50-mg Bond Elut-ENV SPE cartridge (previously  
226 conditioned with 1 mL of dichloromethane, 1 mL of methanol and 1 mL of water). Mercaptans  
227 retained are directly derivatized by passing 1 mL of an aqueous solution of DBU (6.7%) and  
228 50 µL of a 2000 mg L<sup>-1</sup> solution of mercaptoglycerol on 6.7% DBU aqueous solution. The  
229 cartridge was imbibed with the reagents during 20 min at room temperature. Then, the  
230 cartridge is first washed with a solution of 0.2 H<sub>3</sub>PO<sub>4</sub> with 40% methanol and finally with 1  
231 mL MilliQ water. Finally, derivatized analytes were eluted with 600 µL of hexane/diethyleter  
232 (75/25) and spiked with 375 ng L<sup>-1</sup> of octafluoronaftalene (internal standard). The eluate was  
233 washed 5 times with 1 mL of a NaCl solution (200 g L<sup>-1</sup>) and finally dried with Na<sub>2</sub>SO<sub>4</sub>  
234 anhydrous. Twenty microlitres of this sample were injected in a Shimazu GCMS-QP2010  
235 Plus gas chromatograph coupled to a quadrupole mass spectrometric detector. Injection  
236 conditions: initial temperature 65°C and after 25 s it was heated up to 260°C (16°C s<sup>-1</sup>) until  
237 the end of the analysis. Carrier gas: He (4.15 min at 2.69 mL min<sup>-1</sup> and then at 1.44 mL min<sup>-1</sup>)  
238 <sup>1</sup>). The column was a DB5-MS (Agilent J&W Scientific): 20m x 0.18mm ID and 0.18 µm  
239 film thickness. The initial column temperature was 40°C for 4 min, heated to 140°C at 25°C  
240 min<sup>-1</sup>, then to 180°C at 15°C min<sup>-1</sup>, afterwards to 210°C at 30°C min<sup>-1</sup> and finally to 280°C at  
241 250°C min<sup>-1</sup>, remaining 10 min at this temperature. Temperatures of the ion source and  
242 interface were kept at 220°C and 270°C, respectively. To obtain the concentration data, the  
243 corresponding analyte peak relative areas to a selected internal standard was calculated.

244 Quantitative analysis of volatile sulphur compounds was performed based on the method  
245 described by Lopez, Aznar, Cacho and Ferreira (2002). The method dilutes the sample in  
246 brine, and the sample headspace is preconcentrated with automated headspace solid-phase  
247 microextraction (HS-SPME) with a CAR-PDMS fiber and subsequently analysed by gas

248 chromatography-pulsed flame photometric detection (GC-PFPD). Therefore, a VARIAN CP-  
249 3800 chromatograph was employed. The column was a DB-WAX ETR (Agilent J&W  
250 Scientific): 30m x 0.31mm ID and 1  $\mu\text{m}$  film thickness. The carrier was He at 2 mL  $\text{min}^{-1}$ . The  
251 temperature program was as follows: 35°C for 5 min, raised at 10°C  $\text{min}^{-1}$  up to 100°C, and  
252 finally raised at 20°C  $\text{min}^{-1}$  up to 220°C. The detector was kept at 300°C. Analytes were  
253 referred to a selected internal standard, response factor was the selected method for the  
254 calibration.

#### 255 2.1.3.4. Quantitative analysis of elements by ICP-OES

256 Microwave assisted digestion in a closed vessel was used to mineralize wine samples.  
257 Samples were further analysed by inductively coupled plasma optical emission spectrometry  
258 (ICP-OES), as described by Gonzalvez, Armenta, Pastor and de la Guardia (2008).  
259 Phosphorus (P) along with ten metals (Al, Cu, Mg, Si, Mn, Fe, Zn, Ca, Na and K) were  
260 quantified. For calibration purposes, stock solutions of a multielemental standard solution  
261 (1000  $\mu\text{g mL}^{-1}$ ) containing elements dissolved in 5%  $\text{HNO}_3$  were prepared. For microwave-  
262 assisted digestion of wine, a microwave system CEM Mars Xpress (Orsay, France) was used.  
263 After sample digestion, they were injected in a Thermo Elemental IRIS Intrepid spectrometer  
264 (MA, USA). The carrier gas employed was Argon.

#### 265 2.1.4. Data analysis

##### 266 2.1.4.1. Minerality rating

267 Two-way ANOVAs with assessors as random factor and the river bank (left vs. right) as fixed  
268 factor were calculated on the scores of minerality (the average minerality score of the two  
269 replications) under the two conditions separately: (i) orthonasal olfaction alone and (ii) global  
270 tasting.

##### 271 2.1.4.2. Free description task

272 Descriptors that referred to the same semantic universe were combined to form categories  
273 through a triangulation categorization process. Three researchers participated in this step, each  
274 forming separately their categories. The categories of the three researchers were then  
275 compared and the final categories decided consensually.

276 Correspondence Analysis (CA) was performed on the wine (8) x aroma attributes (16)  
277 contingency table each cell in this table represents the frequency of citation (FC) for a term in  
278 a wine. To limit noise in the CA and highlight the main sensory characteristics of the wines  
279 only attributes cited by at least two participants were included in the contingency table  
280 Average perceived minerality intensity scored by experts was added as a continuous  
281 supplementary variable and river bank (left or right) as a nominal supplementary variable.

#### 282 2.1.4.3. Chemical data

283 For all conventional parameters, the average of the two replicates was computed. Quantitative  
284 volatile compounds data presented Table 2 were transformed into Odour Activity Values  
285 (OAV) by dividing them by their corresponding sensory thresholds (ST). In the case of  
286 concentrations under detection (DL) or quantification (QL) limits, OAV was calculated as  
287 DL/ST or QL/ST, respectively (San Juan, Cacho, Ferreira & Escudero, 2011). In order to rank  
288 compounds in accordance to their discriminatory power the quotients between the maximum  
289 and minimum OAV were calculated for each compound. In case of  $OAV_{min} < 0.2$ , OAV  
290 min was arbitrary assigned a value of 0.2 for avoiding quotients with no sense from a sensory  
291 point of view, especially when  $OAV_{min}$  was zero as suggested by San Juan, Cacho, Ferreira  
292 & Escudero (2011).

293 Fourteen aroma vectors were built (supplementary material 2) by combining the OAV of  
294 odorants with similar chemical and sensory properties (Loscos, Hernandez-Orte, Cacho &  
295 Ferreira, 2007; Sáenz-Navajas et al, 2015). First the individual OAV of all compounds were  
296 calculated and then the OAV of the compounds belonging to each aroma vector were added to

297 build the 14 aroma vectors. Acetaldehyde was not included in any vector and was individually  
298 considered given its particular sensory properties.

299 A one-way ANOVA was performed with the river bank as fixed factor and aroma vectors and  
300 compounds as quantitative variables.

#### 301 *2.1.4.4. Link between sensory and chemical variables*

302 Pearson correlation coefficients ( $r$ ) were calculated for the eight wines between 1) the  
303 averaged (across all assessors) minerality scores and the concentration value of individual  
304 compounds and 2) the averaged minerality scores and chemical variables (including 14 aroma  
305 vectors, the concentration of phosphorus and the 10 metal determined as well as and  
306 conventional oenological variables).

307 In order to simplify the interpretation and presentation of results a Principal Component  
308 Analysis (PCA) was calculated with chemical variables presenting Pearson correlation  
309 coefficients of at least 0.30 as active variables. To evaluate the link between chemical  
310 compounds and sensory data both the frequency scores of the attributes obtained during the  
311 free description, and the experts average minerality score were projected as illustrative  
312 variables. The statistical analyses were carried out with XLSTAT software (Version  
313 2014.2.02).

### 314 *2.2. Evaluation of the sensory impact of MeSH in wine models*

#### 315 *2.2.1. Preparation of wine models (WM)*

316 A wine model was prepared by mixing a pool of common wine compounds (see  
317 supplementary material 4) as described elsewhere (Franco-Luesma, Sáenz-Navajas, Valentin,  
318 Ballester, Rodrigues & Ferreira, 2016) and at concentration ranges within the natural ranges  
319 of occurrence in Chardonnay wines (Herrero et al., 2016). This WM reproduce the aroma  
320 characteristics of a white wine (detailed compositional data are provided in supplementary

321 material 3). The sensory role played by MeSH was studied by spiking at four levels of  
322 concentration (0, 0.8, 1.6 and 3.2  $\mu\text{g L}^{-1}$ ) the WM.

### 323 *2.2.2. Sensory evaluation of WMs*

324 A total of 16 staff members (51.8% men and 48.2% women from 19 to 67 years, median of  
325 39.5 years) from the Laboratory for Analysis of Aroma and Enology (LAAE) completed one  
326 session. They were wine experts with wide experience in aroma description of wine aroma.

327 Twenty-five-mL samples were presented at room temperature in black ISO glasses covered  
328 with plastic Petri dishes and identified only by random three-digit codes following a random  
329 arrangement, different for each judge. Participants were presented with four WMs containing  
330 different levels of MeSH (0, 0.8, 1.6 and 3.2  $\mu\text{g L}^{-1}$ ). They were asked to smell the four  
331 samples orthonasally from left to right and score the intensity of six attributes (smoky,  
332 gunflint, shellfish, chalky, white fruit and floral) on a 10-cm unstructured -linear scale  
333 anchored with the words “absence” and “high intensity” on the left and right ends,  
334 respectively..

### 335 *2.2.3. Data analysis*

336 Two-way ANOVAs (judges as random and wines as fixed factors) were calculated for each of  
337 the six descriptors evaluated. Student–Newmans–Keuls post hoc pairwise comparisons (95%)  
338 were carried when a wine significant effect was observed.

## 339 **3. Results and discussion**

### 340 *3.1 Minerality judgment*

341 The ANOVA showed no effect of river bank on minerality scores in the global tasting  
342 condition. In contrast a significant effect was observed in the orthonasal olfaction condition,

343 ( $F = 7.338$ ;  $P < 0.007$ ). Samples from the left bank were found more mineral ( $3.3 \pm 0.1$ ) than  
344 those from the right bank ( $3.0 \pm 0.2$ )

345 The lack of significant difference in the global tasting condition is in apparent contradiction  
346 with other works that report a link between minerality and tastes such as sourness or bitterness  
347 (Heymann et al., 2014; Ballester et al., 2013). Interestingly, Ballester et al. (2013) found that  
348 minerality scores evaluated in the presence of exclusively orthonasal aroma were not  
349 significantly correlated with scores evaluated under global conditions. These authors  
350 suggested that two types of minerality concepts could appear in the presence of different  
351 sensory stimuli, which could explain why participants found differences in minerality  
352 evaluated under orthonasal olfaction alone but not under global tasting.

353 The effect of river bank on olfactory minerality indicates that the position of vines in relation  
354 to the river may be one of the factors that contribute to the emergence of the olfactory  
355 component of minerality in Chablis wines. In line with this interpretation Bramley &  
356 Hamilton (2007) concluded that vineyards producing wines that are deemed characteristic of a  
357 region may in fact be capable of producing quite contrasting wines. Thus, topoclimatic  
358 variability, as is the case in the left and right serein banks in Chablis, seems to have an  
359 influence on wine style, in our case, on perceived minerality.

### 360 *3.2. Sensory differences among wines from different river bank*

361 The terms “floral” and “mineral” were the most cited by participants (cited by a maximum of  
362 30% of participants in both cases) when characterizing the wines. Wines from the *climats*  
363 Vaucoupin and Montée de Tonnerre, both from the right side of the river, presented the  
364 highest citations for the floral term (28% and 20%, respectively), while Côte de Léchet and  
365 Beauroy, both from the left side, accounted for the highest citations (30% and 22%) for the  
366 mineral term. These results would firstly suggest that the term mineral is naturally used by



367 winemakers in the Chablis region and secondarily that the mineral wines would be opposed to  
368 floral wines.

369 The CA plot derived from the orthonasal aroma characterization is shown in Figure 2. The  
370 first CA dimension explains 27.57% of variance. On this dimension, gunflint, sulphur and  
371 wood are in opposition to floral, spicy, sweet aroma, yellow/tropical fruits and undergrowth  
372 aroma descriptors. The second dimension which is negatively correlated with the mineral  
373 intensity score ( $r = -0.53$ ) explains 20.95% of variance. The barycenters of the left (bottom  
374 part of the plot) and right (top part of the plot) river bank wines (projected as supplementary  
375 nominal variable) “river bank” are opposed on this dimension thus showing an opposition  
376 between wines derived from grapes grown on the left and right bank of the river.  
377 Interestingly, the attributes minerality (19%), freshness/mint (16%) and gunflint (12%) are the  
378 main contributors to the second dimension and thus to minerality, which is in clear opposition  
379 to floral, spicy, yellow/tropical fruits and sweet aroma terms. These results are mainly in  
380 agreement with previous data observed by Heymann et al. (2014), Parr et al. (2015) and  
381 Ballester et al. (2013). It is interesting to remark that wines from the right side of the river  
382 (lower minerality scores) present the highest frequency of citations for all attributes employed  
383 by at least two participants (citrus, wood, floral, white fruit, yellow/tropical fruits, and  
384 sulphur), except for the descriptor minerality, which was mostly employed for describing  
385 wines from the left side of the river (higher minerality scores). This result is in agreement  
386 with the results observed by Parr et al. (2015), which suggested that the absence of overall  
387 aroma could lead to enhanced judgment of minerality.

### 388 *3.3. Relationship between chemical composition and minerality ratings*

389 The study of volatile composition of the eight wines has provided quantitative data for 73  
390 compounds belonging to several important families of wine aroma (Table 2). Pearson  
391 correlation coefficients show that ten compounds were significantly ( $P < 0.05$ ) correlated with

392 the minerality score. Among them, four were positively correlated (methanethiol, ethyl  
393 acetate, acetic acid and  $\gamma$ -decalactone) and six negatively (isoamyl acetate, hexyl acetate,  $\beta$ -  
394 damascenone, ethyl cinnamate, ethyl dihydroxycinnamate and linalool). Compounds present  
395 at concentrations lower than their sensory threshold are not expected to have an important  
396 sensory impact on the sensory properties of wines, which suggests that hexyl acetate  
397 (maximum concentration 13 times lower than its sensory threshold) and linalool (maximum  
398 concentration five times lower than its sensory threshold) would have a negligible effect on  
399 perceived minerality. However, it cannot be ruled out that compounds at concentration levels  
400 below their sensory threshold would not contribute to the aroma formation of the studied  
401 wines, especially for compounds sharing chemical structure and aroma properties. Such  
402 groups of compounds are thought to act additively together and exert a cooperative effect to  
403 form an aroma descriptor (see for instance Loscos et al., 2007).

404 Table 3 shows solely the chemical variables (OAVs of the 14 aroma vectors and on the  
405 individual volatiles not included in the vectors, as well as the metals and the conventional  
406 parameters) that presented significant effects ( $P < 0.05$ ) for the river bank in the ANOVAs.  
407 Methanethiol was significantly higher in wines from the left side of the river ( $3.0 \pm 0.5 \mu\text{g L}^{-1}$ )  
408 than from the right ( $1.8 \pm 0.6 \mu\text{g L}^{-1}$ ). The opposite was observed for norisoprenoid vector (left:  
409  $\text{OAV}_{\text{average}} 59.2 \pm 1.93$ ; right:  $\text{OAV}_{\text{average}} 69.4 \pm 5.91$ ) and copper (left: average  $0.19 \pm 0.03 \mu\text{g L}^{-1}$ ;  
410 right: average  $0.29 \pm 0.06 \mu\text{g L}^{-1}$ ) levels, which were higher in wines from the right side. No  
411 significant effect of river bank was observed on conventional parameters. These results show  
412 an effect of the side of the river on the concentration of MeSH (higher on the left side),  
413 norisoprenoids ( $\beta$ -damascenone,  $\beta$ -ionone and  $\alpha$ -ionone) and copper (higher in the right side).

414 *3.4. Relationship between chemical composition, sensory description and minerality scores*

415 In an attempt to further understand the link between chemical variables differing between the  
416 river banks (MeSH, norisoprenoids and copper) and sensory variables, a PCA was calculated  
417 with chemical parameters as active variables and sensory (intensity score of minerality and  
418 descriptive terms) as illustrative variables (Figure 3). At first sight the significant correlation  
419 ( $P < 0.05$ ) observed between MeSH and the attribute shellfish/chalky ( $r = 0.77$ ) may be  
420 surprising because this sulphur-containing compound has been described to be involved in the  
421 formation of cooked cabbage, camembert, or reductive aroma in white wines (Mestres, Busto  
422 & Guasch, 2000; Franco-Luesma et al., 2016). However, these works deal with concentrations  
423 even 15 times higher (i.e.  $55 \mu\text{g L}^{-1}$  in Franco-Luesma et al., 2016 and  $16 \mu\text{g L}^{-1}$  in Mestres,  
424 Busto & Guasch, 2000) than those found in the Chardonnays of the present study (range of  
425  $1.4\text{-}3.5 \mu\text{g L}^{-1}$ ). This together with the fact that this sulphur compound has been described to  
426 be an important contributor to the characteristic aroma of cooked shellfish (Josephson, 1991;  
427 Sekiwa, Kubota & Kobayashi, 1997; Baek & Cadwallader, 1997), suggests that MeSH could  
428 be involved in the formation of shellfish aroma of the studied wines. To confirm such  
429 hypothesis, an independent study was carried out by preparing white wine models similar to  
430 those of the study and spiked with four different levels of MeSH (level 0:  $0 \mu\text{g L}^{-1}$ , level 1:  
431  $0.8$ , level 2:  $1.6$ , level 3:  $3.2 \mu\text{g L}^{-1}$ ) covering the concentration range found in the studied  
432 wines. A panel of wine experts evaluated the intensity of the six attributes found to be mainly  
433 related to MeSH concentrations as shown in Figure 3 (positively: smoky, gunflint, shellfish  
434 and chalky; negatively: white fruits and floral). Results showed that wines spiked with  $3.2 \mu\text{g}$   
435  $\text{L}^{-1}$  of MeSH were perceived significantly more intense in shellfish aroma ( $P < 0.01$ ) and less  
436 intense in white fruits and floral descriptors ( $P < 0.05$ ) than wines containing lower levels ( $0\text{-}$   
437  $1.6 \mu\text{g L}^{-1}$ ) (see supplementary material 5). This result would support the idea that MeSH can

438 exert a suppressor effect on positive aromas such fruity or floral, which would induce an  
439 absence of overall positive aroma as suggested by Parr et al. (2015).

440 Further, it is interesting to comment the inverse correlation found between copper  
441 concentration and MeSH ( $r=-0.68$ ) as well as minerality scores ( $r=-0.60$ ) (Figure 3). Recently,  
442 Franco-Luesma and Ferreira (2014) reported the existence of strong interactions in wine  
443 matrix between  $\text{Cu}^{+2}$  and  $\text{H}_2\text{S}$  and MeSH, leading to the formation of odourless MeSH-Cu  
444 complexes. Thus, the higher the copper concentration in wines, the less the concentration of  
445 the free sensory-active form of MeSH is. This would explain the fact that more mineral wines  
446 have higher concentrations of MeSH (as they present higher shellfish aroma) and less Cu  
447 concentration (Table 3). This would support an indirect relationship between copper levels  
448 and minerality scores.

449 Concerning the norisoprenoid vector, it is a vector formed by  $\beta$ -damascenone, which is  
450 usually described to elicit fruity or backed apple aromas, and  $\alpha$ - and  $\beta$ -ionones, presenting a  
451 violet-like aroma. The sensory role of this vector in wines has been widely demonstrated and  
452 it has been described to be an important contributor to floral, fresh or dried fruity aroma of  
453 wines depending on its concentration (San Juan, Ferreira, Cacho, & Escudero, 2011; López,  
454 Ezpeleta, Sánchez, Cacho, & Ferreira, 2004). This would support the fact that this vector is  
455 positively correlated especially with the descriptor white fruits as well as to floral, and  
456 negatively linked to minerality scores (Table 3 and Figure 3).

## 457 **Conclusions**

458 This article measures the effect of the banks of the *Serein* river on the intensity and the  
459 sensory and chemical drivers of wine minerality aroma. **The results answer our two questions:**  
460 **Firstly**, wines belonging to the left side of the bank were scored higher in minerality than  
461 wines from the right side. **Secondly**, methanethiol, which is involved in the shellfish aroma  
462 and exerts a masking effect on floral and fruity nuances, is present at higher concentrations in

463 wines from the left (more mineral) than from the right side of the river. Contrary,  
464 norisoprenoids, responsible for white fruit and floral aromas, and copper levels, linked to  
465 lower levels to free MeSH, are at higher concentrations in wine from the right (less mineral)  
466 than from the left side. However further work is needed to verify whether these results would  
467 generalize to other vintages

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476

#### 477 **References**

478

479 Baek, H. H.; Cadwallader, K. R. In *Flavor and Lipid Chemistry of Seafoods*; Shahidi, F.,  
480 Cadwallader, R., Eds.; ACS Symposium Series 674; American Chemical Society:  
481 Washington, DC, 1997; pp 85–94.

482

483 Ballester, J., Mihnea, M., Peyron, D., & Valentin, D. (2013). Exploring minerality of  
484 Burgundy Chardonnay wines: A sensory approach with wine experts and trained panelists.  
485 *Australian Journal of Grape and Wine Research*, 19, 140–152.

486

487 Baroň, M., & Fiala, J. (2012). Chasing after minerality, relationship to yeast nutritional stress  
488 and succinic acid production. *Czech Journal of Food Sciences*, 30, 188-193.

489

490 Bramley, R. G. V. *Progress in the development of precision viticulture-Variation in yield,*  
491 *quality and soil properties in contrasting Australian vineyards.* No. 14. Occasional report,  
492 2001.

493

494 Bramley, R. G. V., & Hamilton, R. P. (2007). Terroir and precision viticulture: Are they  
495 compatible? *Journal International des Sciences de la Vigne et du Vin*, 41, 1.

496

497 Cannard, H. (1999). *Les vignobles de Chablis et de l'Yonne: réédition, après actualisation, de*  
498 *Balades en Bourgogne, guide consacré aux vignobles de Chablis et de l'Auxerrois.* Cannard.

499

500 Cahier des charges de l'Appellation d'Origine Contrôlée « Chablis Premier Cru ». 2012.  
501 Journal Officiel de la République Française. 11.04.2012.

502

503 Deneulin, P., & Bavaud, F. (2016). Analyses of open-ended questions by renormalized  
504 associativities and textual networks: A study of perception of minerality in wine. *Food*  
505 *Quality and Preference*, 47, 34-44.

506

507 Ferreira, V., Sáenz-Navajas, M. P., Campo, E., Herrero, P., de la Fuente, A., & Fernández-  
508 Zurbano, P. (2016). Sensory interactions between six common aroma vectors explain four  
509 main red wine aroma nuances. *Food Chemistry*, 199, 447-456.

510

511 Fourment, M., Ferrer, M., González-Neves, G., Barbeau, G., Bonnardot, V., & Quénot, H.  
512 (2013). Spatial variability of temperature and grape berry composition at terroir scale in  
513 Uruguay. *Ciencia y Técnica Vitícola*, 329-334.

514

515 Franco-Luesma, E., Sáenz-Navajas, M. P., Valentin, D., Ballester, J., Rodrigues, H., &  
516 Ferreira, V. Study of the effect of H<sub>2</sub>S, MeSH and DMS on the sensory profile of wine model  
517 solutions by Rate-All-That-Apply (RATA). *Food Research International*, 87, 152-160.

518

519 Franco-Luesma, E., & Ferreira, V. (2014). Quantitative analysis of free and bonded forms of  
520 volatile sulfur compounds in wine. Basic methodologies and evidences showing the existence  
521 of reversible cation-complexed forms. *Journal of Chromatography A*, 1359, 8-15.

522

523 Gonzalvez, A., Armenta, S., Pastor, A., & de la Guardia, M. Searching the most appropriate  
524 sample pretreatment for the elemental analysis of wines by inductively coupled plasma-based  
525 techniques. *Journal of Agricultural and Food Chemistry*. 2008, 56, 4943–4954.

526

527 Herrero, P., Sáenz-Navajas, P., Culleré, L., Ferreira, V., Chatin, A., Chaperon, V., Litoux-  
528 Desrues, F. & Escudero, A. (2016). Chemosensory characterization of Chardonnay and Pinot  
529 Noir base wines of Champagne. Two very different varieties for a common product. *Food*  
530 *chemistry*, 207, 239-250.

531

532 Heymann, H., Hopfer, H., & Bershaw, D. (2014). An exploration of the perception of  
533 minerality in white wines by projective mapping and descriptive analysis. *Journal of Sensory*  
534 *Studies*, 29, 1-13.

535

536 Josephson, D. B. (1991). Seafood. In H. Maarse (Ed.), *Volatile compounds in foods and*  
537 *beverages* (pp. 179–202). (1st ed.). New York: Marcel Dekker Inc

538

539 Liu, J., Toldam-Andersen, T. B., Petersen, M. A., Zhang, S., Arneborg, N., & Bredie, W. L.  
540 (2015). Instrumental and sensory characterisation of Solaris white wines in Denmark. *Food*  
541 *chemistry*, 166, 133-142.

542

543 Lopez, R., Aznar, M., Cacho, J., & Ferreira, V. (2002). Determination of minor and trace  
544 volatile compounds in wine by solid-phase extraction and gas chromatography with mass  
545 spectrometric detection. *Journal of Chromatography A*, 966(1), 167-177.

546

547 López, R., Ezpeleta, E., Sánchez, I., Cacho, J., & Ferreira, V. (2004). Analysis of the aroma  
548 intensities of volatile compounds released from mild acid hydrolysates of odourless  
549 precursors extracted from Tempranillo and Grenache grapes using gas chromatography-  
550 olfactometry. *Food Chemistry*, 88(1), 95-103.

551

552 Loscos, N., Hernandez-Orte, P., Cacho, J., & Ferreira, V. (2007). Release and formation of  
553 varietal aroma compounds during alcoholic fermentation from nonfloral grape odorless flavor  
554 precursors fractions. *Journal of Agricultural and Food Chemistry*, 55(16), 6674-6684.

555

556 Maltman, A. (2013). Minerality in wine: a geological perspective. *Journal of Wine Research*,  
557 24, 169–181.

558



559 Mateo-Vivaracho, L., Cacho, J., & Ferreira, V. (2008). Improved solid-phase extraction  
560 procedure for the isolation and in-sorbent pentafluorobenzyl alkylation of polyfunctional  
561 mercaptans: Optimized procedure and analytical applications. *Journal of Chromatography A*,  
562 *1185*, 9-18.

563

564 Mestres, M., Busto, O., & Guasch, J. (2000). Analysis of organic sulfur compounds in wine  
565 aroma. *Journal of chromatography A*, *881*, 569-581.

566

567 Noble, A. C., Arnold, R. A., Masuda, B. M., Pecore, S. D., Schmidt, J. O., & Stern, P. M.  
568 (1984). Progress towards a standardized system of wine aroma terminology. *American*  
569 *Journal of Enology and Viticulture*, *35*, 107-109.

570

571 Ortega, C., López, R., Cacho, J., & Ferreira, V. (2001). Fast analysis of important wine  
572 volatile compounds: Development and validation of a new method based on gas  
573 chromatographic–flame ionisation detection analysis of dichloromethane microextracts.  
574 *Journal of Chromatography A*, *923*, 205-214.

575

576 Parr, W. V., Ballester, J., Peyron, D., Grose, C., & Valentin, D. (2015). Perceived minerality  
577 in Sauvignon wines: Influence of culture and perception mode. *Food Quality and Preference*,  
578 *41*, 121–132.

579

580 Parr, W. V., Valentin, D., Breitmeyer, J., Peyron, D., Darriet, P., Sherlock, R., Robinson, B.,  
581 Grose, C., & Ballester, J. (2016). Perceived minerality in Sauvignon blanc wine: Chemical  
582 reality or cultural construct?. *Food Research International*, *87*, 168-179.

583

584 Rodrigues, H., Ballester, J., Sáenz-Navajas, M. P., & Valentin, D. (2015). Structural approach  
585 of social representation: Application to the concept of wine minerality in experts and  
586 consumers. *Food Quality and Preference*, *46*, 166-172.

587

588 Sáenz-Navajas, M. P., Avizcuri, J. M., Ballester, J., Fernández-Zurbano, P., Ferreira, V.,  
589 Peyron, D., & Valentin, D. (2015). Sensory-active compounds influencing wine experts' and  
590 consumers' perception of red wine intrinsic quality. *LWT-Food Science and Technology*, *60*,  
591 400-411.

592

593 San Juan, F., Ferreira, V., Cacho, J., & Escudero, A. (2011). Quality and aromatic sensory  
594 descriptors (mainly fresh and dried fruit character) of Spanish red wines can be predicted



595 from their aroma-active chemical composition. *Journal of Agricultural and Food Chemistry*,  
596 59, 7916-7924.

597

598 Sekiwa, Y., Kubota, K., & Kobayashi, A. (1997). Characteristic flavor components in the  
599 brew of cooked clam (*Meretrix lusoria*) and the effect of storage on flavor formation. *Journal*  
600 *of Agricultural and Food Chemistry*, 45, 826-830.

601

602 Van Leeuwen, C., & Seguin, G. (2006). The concept of terroir in viticulture. *Journal of Wine*  
603 *Research*, 17(1), 1-10.

604

605 Van Leeuwen, C., Friant, P., Chone, X., Tregoat, O., Koundouras, S., & Dubourdieu, D.  
606 (2004). Influence of climate, soil, and cultivar on terroir. *American Journal of Enology and*  
607 *Viticulture*, 55(3), 207-217.

608

609 Van Leeuwen, C., & Seguin, G. (1994). Incidences de l'alimentation en eau de la vigne,  
610 appréciée par l'état hydrique du feuillage, sur le développement de l'appareil végétatif et la  
611 maturation du raisin (*Vitis vinifera* variété Cabernet franc, Saint-Emilion, 1990). *Journal*  
612 *International des Sciences de la Vigne et du Vin*, 28, 81-110.

613

614 **Figure Captions**

615 **Figure 1.** Projection of the eight *climats* (4 from the left side and four from the right side).

616 **Figure 2.** Projection of aroma descriptors and wines (samples from the right side are  
617 underlined) from different *climat* origin on the Correspondence Analysis (CA) space  
618 (dimensions 1 and 2). The arrow (quantitative illustrative variable) shows the projection of the  
619 minerality score given by assessors. Side of the river (right and left side) is projected as  
620 nominal illustrative variable.

621 **Figure 3.** Projection of a) aroma vectors (active variables) and b) wines (wines from the right  
622 side are in blue and underlined, those from the left are in red) from different *climat* origin on  
623 the Principal Component Analysis (PCA) space (dimensions 1 and 2). The arrow (quantitative  
624 illustrative variable) shows the projection of the minerality score given by assessors. Sensory  
625 descriptors derived from free descriptive task are projected as nominal illustrative variables.

626

627

**Table 1.** Sample information and basic compositional data the wines studied.

	River bank side	Alcohol % (v/v)	pH	Volatile acidity (g L <sup>-1</sup> ) <sup>a</sup>	Titrateable acidity (g L <sup>-1</sup> ) <sup>b</sup>	Reducing sugars (g L <sup>-1</sup> )	Lactic acid (g L <sup>-1</sup> )	Malic acid (g L <sup>-1</sup> )	Free SO <sub>2</sub> (mg L <sup>-1</sup> )	Total SO <sub>2</sub> (mg L <sup>-1</sup> )
Montmains	Left	13.8	3.29	0.31	6.4	1.95	1.4	0.6	21.6	96.4
Vaillons	Left	13.8	3.39	0.26	5.4	2.42	1.5	0.3	30.8	103.2
Beuroy	Left	13.8	3.35	0.27	6.0	1.95	1.4	0.4	29.2	132.8
Côte de Léchet	Left	13.9	3.34	0.28	6.0	2.16	1.6	0.2	19.6	103.2
Fourchaume	Right	13.8	3.37	0.29	6.2	1.82	1.6	0.3	23.2	88.0
Vaucopin	Right	13.8	3.32	0.22	6.0	2.05	1.6	0.1	32.8	98.8
Mont de Milieu	Right	13.7	3.35	0.23	5.8	1.81	1.6	0.1	27.6	99.6
Montée de Tonnerre	Right	13.7	3.39	0.26	5.3	1.72	1.5	0.2	14.8	87.2

<sup>a</sup>Expressed as g L<sup>-1</sup> of acetic acid.<sup>b</sup>Expressed as g L<sup>-1</sup> of tartaric acid

**Table 2.** Limit of detection (LOD), chemical standards purchased in, sensory thresholds, concentration ranges and average values of volatiles found in the set of the 8 wines (all expressed in micrograms per liter). Differentiation ability calculated as the quotient between maximum and minimum concentrations (Max/Min) and correlation coefficients (r) of linear regression between the concentration of each compound and minerality scores evaluated by experts. Compounds significantly correlated to minerality scores and present at concentrations above their sensory threshold are marked in bold.

compounds	LOD	chemical standard	sensory threshold <sup>a</sup>	range	average	max/min	r
<b>ACETATES</b>							
2-methylpropyl acetate	0.10	Chem Service	1600	6.0-9.9	7.5	1.7	-0.52
butyl acetate	0.16	Fluka	1800	2.3-6.0	3.4	2.6	-0.60
phenylethyl acetate	0.00	Chem Service	250	16.6-33.7	25.0	2.0	-0.46
<b>ethyl acetate</b>	10	Aldrich	<b>12300</b>	<b>44267-74290</b>	<b>56507</b>	<b>1.7</b>	<b>0.80</b>
<b>isoamyl acetate</b>	20	Chem Service	<b>30</b>	<b>665-1696</b>	<b>1075</b>	<b>2.6</b>	<b>-0.76</b>
hexyl acetate	10	Chem Service	1500	54.3-116	83.0	2.1	-0.75
<b>ACIDS</b>							
<b>acetic acid</b>	8920	Panreac	<b>300000</b>	<b>223556-396360</b>	<b>316217</b>	<b>1.8</b>	<b>0.71</b>
butyric acid	95	Polyscience	173	1031-1385	1236	1.3	0.21
2-methylpropanoic acid	100	Aldrich	2300	1396-2563	1802	1.8	-0.47
2-methylbutanoic acid	24	Aldrich	33	637-875	726	1.4	-0.19
hexanoic acid	16	Polyscience	420	5018-6038	5557	1.2	0.24
octanoic acid	9	Fluka	500	12695-17491	14622	1.4	0.45
decanoic acid	24	Polyscience	1000	1719-3311	2401	1.9	-0.46
<b>ALCOHOLS</b>							
2-methyl-1-propanol	24	Merk	40000	13647-28676	20669	2.1	-0.02
1-butanol	3	Aldrich	150000	600-1358	881	2.3	-0.17
3-methyl-1-butanol	19	Aldrich	30000	133855-184227	16324	1.4	0.20
1-hexanol	4	Sigma	8000	1198-1543	1380	1.3	-0.17
Z-3-hexenol	12	Aldrich	400	196-238	211	1.2	-0.02
methionol	17	Aldrich	1000	347-1289	553	3.7	-0.26
benzyl alcohol	6	Aldrich	200000	202-462	263	2.3	0.38
β-phenylethanol	5	Fluka	14000	10917-20970	14808	1.9	-0.07
<b>CARBONYLIC COMPOUNDS</b>							
benzaldehyde	0.01	Fluka	2000	12.1-23.5	18.0	1.9	-0.30
<b>β-damascenone</b>	0.15	Firmenich	<b>0.05</b>	<b>2.8-3.8</b>	<b>3.2</b>	<b>1.4</b>	<b>-0.75</b>
α-ionone	0.01	Sigma	2.6	<0.01-0.17	0.09	16.8	-0.21
β-ionone	0.04	Sigma	0.09	0.07-0.11	0.09	1.4	0.07
acetaldehyde	90	Aldrich	500	607-1123	891	1.8	-0.09
diacetyl	500	Aldrich	100	<500			
acetoin	180	Aldrich	150000	2180-5958	3875	2.7	0.22
syringaldehyde	0.01	Aldrich	50000.0	<0.01-0.45	0.21	44.7	-0.07

compounds	LOD	chemical standard	sensory threshold	range	average	Max/Min	r <sup>c</sup>
<b>ESTERS</b>							
ethyl propanoate	50	Fluka	5500	<50-139	63.6	2.8	0.36
ethyl butyrate	30	Aldrich	125	324-447	380	1.4	0.41
ethyl hexanoate	30	PolyScience	62	1291-1910	1565	1.5	-0.02
ethyl octanoate	20	PolyScience	580	1803-2558	2187	1.4	0.03
ethyl decanoate	20	PolyScience	200	207-271	241	1.3	0.05
ethyl lactate	10	Aldrich	154000	198466-246761	228376	1.2	0.39
diethyl succinate	20	Fluka	200000	2192-5224	3056	2.4	-0.24
ethyl 2-methylpropanoate	0.57	Aldrich	15	71.7-233	148	3.2	0.39
ethyl 2-methylbutyrate	0.02	Fluka	18.0	8.6-14.1	11.5	1.6	0.12
ethyl 3-methylbutyrate	0.48	Fluka	3.0	16.2-30.6	23.7	1.9	0.12
<b>ethyl cinnamate</b>	<b>0.02</b>	Aldrich	<b>1.1</b>	<b>3.8-10.3</b>	<b>5.8</b>	<b>2.7</b>	<b>-0.84</b>
<b>ethyl dihydroxycinnamate</b>	<b>0.01</b>	Fluka	<b>1.6</b>	<b>0.5-2.4</b>	<b>0.9</b>	<b>4.7</b>	<b>-0.86</b>
methyl vanillate	0.02	Lancaster	3000	19.9-23.5	21.2	1.2	-0.66
ethyl vanillate	0.02	Lancaster	990	1.7-3.6	2.5	2.1	-0.61
<b>VOLATILE PHENOLS</b>							
guaiaicol	0.01	Aldrich	9.5	9.9-13.5	11.6	1.4	-0.06
o-cresol	0.19	Aldrich	31.0	0.62-1.18	0.86	1.9	-0.60
4-ethylguaiaicol	0.01	Aldrich	33.0	0.11-0.41	0.24	3.9	-0.19
m-cresol	0.01	Fluka	68.0	0.42-0.60	0.49	1.4	-0.48
4-propylguaiaicol	0.02	Lancaster	10.0	<0.02	<0.02		
eugenol	0.01	Aldrich	6.0	2.3-5.5	3.8	2.4	-0.33
4-ethylphenol	0.02	Aldrich	35.0	0.26-0.47	0.34	1.8	-0.12
4-vinylguaiaicol	0.01	Lancaster	40.0	34.1-51.7	42.6	1.5	-0.04
<i>E</i> -isoeugenol	0.02	Lancaster	6.0	<0.02	<0.02		
2,6-dimethoxyphenol	0.03	Aldrich	570.0	23.4-45.8	35.8	2.0	0.09
4-vinylphenol	0.01	Lancaster	180.0	61.7-128	81.0	2.1	-0.13
4-allyl-2,6-dimethoxyphenol	0.01	Aldrich	1200.0	5.5-9.4	7.2	1.7	-0.35
vanillin	0.01	Aldrich	995.0	7.4-37.2	18.7	5.0	-0.41
acetovanillone	0.02	Aldrich	1000.0	23.9-33.3	28.2	1.4	-0.58
<b>LACTONES</b>							
<i>E</i> -whiskylactone	0.02	Aldrich	790.0	3.4-35.2	20.6	10.3	-0.24
<i>Z</i> -whiskylactone	0.01	Aldrich	67.0	2.6-48.4	27.7	18.6	-0.18
γ-nonalactone	0.01	Aldrich	25.0	3.8-8.0	5.6	2.1	-0.36
<b>γ-decalactone</b>	<b>0.07</b>	Lancaster	<b>0.7</b>	<b>15.7-42.9</b>	<b>30.6</b>	<b>2.7</b>	<b>0.91</b>
γ-butyrolactone	18	Aldrich	35000	6155-6878	6558	1.1	0.04
<b>TERPENOLS</b>							
linalool	0.02	Aldrich	25.0	2.5-4.8	3.4	1.9	-0.78
α-terpineol	0.01	Fluka	250.0	4.0-5.3	4.5	1.3	-0.40
β-citronellol	0.15	Aldrich	100.0	<0.15	<0.15		
geraniol	0.01	Fluka	20.0	<0.01	<0.01		

compounds	LOD	chemical standard	sensory threshold <sup>b</sup>	range	average	Max/Min	r
<b>VOLATILE SULFUR COMPOUNDS</b>							
dimethyl sulfide (DMS)	0.53	Merk	25	5.09-16.3	10.54	3.20	0.19
hydrogen sulfide (H <sub>2</sub> S)	0.01	*	1.1-1.6	0.64-2.01	1.18	3.12	-0.28
<b>methanethiol (MeSH)</b>	<b>0.24</b>	Fluka	<b>1.8- 3.1</b>	<b>1.39-3.45</b>	<b>2.37</b>	<b>2.49</b>	<b>0.76</b>
ethanethiol (EtSH)	0.14	Sigma-Aldrich	1.1	<0.14	<0.14		
<b>POLYFUNCTIONAL MERCAPTANS</b>							
2-methyl-3-furanthiol (MF)	**	**	0.004	0.05-0.09	0.06	1.77	-0.21
2-furfurylthiol (FT)	0.0002	Lancaster	0.0004	0.002-0.008	0.0005	4.20	0.13
4-methyl-4-mercapto-2-pentanone (MP)	0.0020	Alfa Aesar	0.0008	0.002-0.006	0.004	2.62	0.44
3-mercaptohexyl acetate (MHA)	0.0014	Oxford Chemicals	0.004	0.002-0.063	0.013		0.11
3-mercaptohexanol (MOH)	0.0066	Alfa Aesar	0.06	0.26-0.69	0.53	2.61	0.45
benzylmercaptane (BM)	0.0002	Fluka	0.0003	0.002-0.004	0.002	2.22	-0.38

<sup>a</sup>Limit of Detection (LOD) was calculated using  $3 S/m$  ( $S$  is the standard deviation of the response;  $m$  is the slope of the calibration curve).

<sup>b</sup>Odour thresholds (calculated in red wine if available; otherwise threshold in synthetic wine is given). Reference in which the odour threshold value has been calculated is given in brackets. 1: Ferreira et al. (2002), 2: Etievant et al. (1991), 3: Guth (1997), 4: Ferreira et al. (2000), 5: Escudero et al. (2007), 6: Peinado et al. (2004), 7: Escudero et al. (2004), 8: San Juan et al. (2011), 9: Ferreira et al. (2009), 10: López et al. (2002), 11: Boidron et al. (1988), 12: Gemert (2003), 13: Ferreira et al. (2001).

\*H<sub>2</sub>S was produced by addition of an Ar-bubbled water solution of Na<sub>2</sub>S (supplied by Sigma-Aldrich, St. Louis, MO, USA) at pH 9.6

\*\*concentration of MP expressed as micrograms per liter of furfurylthiol (FT)

**Table 3.** Average (and standard deviation) and significance (P) of variables significantly different between wines of the left and right side of the river.

	<b>Left side</b>	<b>Right side</b>	<b>Significance (P)</b>
Minerality score	3.3±0.1	3.0±0.2	0.016
Lactone vector (OAV)	53.9±8.2	34.3±13.7	0.050
Methanethiol vector (OAV)	1.65±0.30	1.00±0.32	0.023
Norisoprenoid vector (OAV)	59.2±1.93	69.4±5.91	0.017
Copper (mg)	19.1±2.6	28.8±6.2	0.027

**Table 2.** Limit of detection (LOD), chemical standards, odour thresholds, correlation coefficients (r) of linear regression between the concentration of each compound and minerality scores evaluated by experts. Average ( $\pm$  standard deviation-sd-) values of volatiles found in the four wines derived from grapes grown in the right and left side of the river (all expressed in micrograms per liter). Compounds significantly correlated to minerality scores and present at concentrations above their sensory threshold are marked in bold.

compounds	LOD <sup>a</sup>	chemical standard	odour threshold <sup>b</sup>	r	Right side	Left side
<b>ACETATES</b>						
2-methylpropyl acetate	0.10	Chem Service	1600 [1]	-0.52	8.1 $\pm$ 1.3	6.8 $\pm$ 1.1
butyl acetate	0.16	Fluka	1800 [2]	-0.60	3.7 $\pm$ 1.5	3.0 $\pm$ 0.6
phenylethyl acetate	0.00	Chem Service	250 [3]	-0.46	25.1 $\pm$ 6.0	24.8 $\pm$ 7.2
<b>ethyl acetate</b>	<b>10</b>	<b>Aldrich</b>	<b>12300 [4]</b>	<b>0.80</b>	<b>50063 <math>\pm</math> 5832</b>	<b>62952 <math>\pm</math> 8385</b>
<b>isoamyl acetate</b>	<b>20</b>	<b>Chem Service</b>	<b>30 [3]</b>	<b>-0.76</b>	<b>1182 <math>\pm</math> 365</b>	<b>968 <math>\pm</math> 226</b>
hexyl acetate	10	Chem Service	1500 [2]	-0.75	92.8 $\pm$ 15.8	73.2 $\pm$ 20.5
<b>ACIDS</b>						
<b>acetic acid</b>	<b>8920</b>	<b>Panreac</b>	<b>300000 [3]</b>	<b>0.71</b>	<b>286315 <math>\pm</math> 76730</b>	<b>346119 <math>\pm</math> 46251</b>
butyric acid	95	Polyscience	173 [5]	0.21	1228 $\pm$ 118	1244 $\pm$ 149
2-methylpropanoic acid	100	Aldrich	2300 [6]	-0.47	2030 $\pm$ 396	1575 $\pm$ 123
2-methylbutanoic acid	24	Aldrich	33 [5]	-0.19	763 $\pm$ 87	689 $\pm$ 36
hexanoic acid	16	Polyscience	420 [5]	0.24	5474 $\pm$ 421	5641 $\pm$ 423
octanoic acid	9	Fluka	500 [5]	0.45	13495 $\pm$ 951	15750 $\pm$ 1734
decanoic acid	24	Polyscience	1000 [5]	-0.46	2910 $\pm$ 520	1893 $\pm$ 119
<b>ALCOHOLS</b>						
2-methyl-1-propanol	24	Merk	40000 [3]	-0.02	21324 $\pm$ 6448	20013 $\pm$ 1657
1-butanol	3	Aldrich	150000 [2]	-0.17	827 $\pm$ 355	934 $\pm$ 84
3-methyl-1-butanol	19	Aldrich	30000 [3]	0.20	154994 $\pm$ 20464	171573 $\pm$ 8530
1-Hexanol	4	Sigma	8000 [3]	-0.17	1429 $\pm$ 118	1331 $\pm$ 91
Z-3-Hexenol	12	Aldrich	400 [3]	-0.02	212 $\pm$ 13	209 $\pm$ 20
methionol	17	Aldrich	1000 [5]	-0.26	626 $\pm$ 444	480 $\pm$ 52
benzyl alcohol	6	Aldrich	200000 [7]	0.38	235 $\pm$ 42	291 $\pm$ 120
$\beta$ -phenylethanol	5	Fluka	14000 [5]	-0.07	14600 $\pm$ 4422	15017 $\pm$ 3241
<b>CARBONYLIC COMPOUNDS</b>						
benzaldehyde	0.01	Fluka	2000 [8]	-0.30	20.4 $\pm$ 3.5	15.7 $\pm$ 5.0
<b><math>\beta</math>-damascenone</b>	<b>0.15</b>	<b>Firmenich</b>	<b>0.05 [3]</b>	<b>-0.75</b>	<b>3.4 <math>\pm</math> 0.3</b>	<b>2.9 <math>\pm</math> 0.1</b>
$\alpha$ -ionone	0.01	Sigma	2.6 [2]	-0.21	0.14 $\pm$ 0.03	0.13 $\pm$ 0.03
$\beta$ -ionone	0.04	Sigma	0.09 [5]	0.07	0.09 $\pm$ 0.01	0.09 $\pm$ 0.01
acetaldehyde	90	Aldrich	500 [3]	-0.09	921 $\pm$ 140	861 $\pm$ 226
diacetyl	50	Aldrich	100 [3]		<500	<500
acetoin	180	Aldrich	150000 [2]	0.22	3351 $\pm$ 891	4400 $\pm$ 1197
syringaldehyde	0.01	Aldrich	50000 [6]	-0.07	0.30 $\pm$ 0.13	0.25 $\pm$ 0.02



compounds	LOD <sup>a</sup>	chemical standard	sensory threshold <sup>b</sup>	r	Right side	Left side
<b>ETHYL/METHYL ESTERS</b>						
ethyl butyrate	30	Aldrich	125 [9]	0.41	353 ± 47	407 ± 35
ethyl hexanoate	30	PolyScience	62 [9]	-0.02	1644 ± 268	1487 ± 168
ethyl octanoate	20	PolyScience	580 [2]	0.03	2303 ± 341	2071 ± 287
ethyl decanoate	20	PolyScience	200 [5]	0.05	249 ± 20	232 ± 28
ethyl lactate	10	Aldrich	154000 [2]	0.39	225087 ± 18083	231665 ± 11687
diethyl succinate	20	Fluka	200000 [2]	-0.24	3449 ± 1421	2662 ± 382
ethyl 2-methylpropanoate	0.57	Aldrich	15 [5]	0.39	143 ± 81	153 ± 19
ethyl 2-methylbutyrate	0.02	Fluka	18 [5]	0.12	12.2 ± 1.8	10.8 ± 2.6
ethyl 3-methylbutyrate	0.48	Fluka	3 [5]	0.12	24.9 ± 4.1	22.5 ± 5.2
ethyl propanoate	50	Fluka	5500 [9]	0.36	<50	77.2 ± 42.0
<b>ethyl cinnamate</b>	0.02	Aldrich	<b>1.1 [5]</b>	<b>-0.84</b>	<b>7.5 ± 3.1</b>	<b>4.2 ± 0.6</b>
<b>ethyl dihydroxycinnamate</b>	0.01	Fluka	<b>1.6 [5]</b>	<b>-0.86</b>	<b>1.3 ± 0.7</b>	<b>0.6 ± 0.1</b>
methyl vanillate	0.02	Lancaster	3000 [10]	-0.66	22.2 ± 0.9	20.3 ± 0.3
ethyl vanillate	0.02	Lancaster	900 [10]	-0.61	2.8 ± 0.6	2.3 ± 0.5
<b>VOLATILE PHENOLS</b>						
guaiacol	0.01	Aldrich	9.5 [5]	-0.06	12.1 ± 1.6	11.1 ± 1.4
o-cresol	0.19	Aldrich	31 [2]	-0.60	1.01 ± 0.14	0.70 ± 0.06
4-ethylguaiacol	0.01	Aldrich	33 [5]	-0.19	0.27 ± 0.13	0.21 ± 0.05
m-cresol	0.01	Fluka	68 [11]	-0.48	0.52 ± 0.05	0.46 ± 0.05
4-propylguaiacol	0.02	Lancaster	10 [10]		<0.02	<0.02
eugenol	0.01	Aldrich	6 [5]	-0.33	4.3 ± 1.4	3.3 ± 0.8
4-ethylphenol	0.02	Aldrich	35 [9]	-0.12	0.37 ± 0.10	0.31 ± 0.02
4-vinylguaiacol	0.01	Lancaster	40 [3]	-0.04	43.6 ± 6.3	41.6 ± 5.7
<i>E</i> -isoeugenol	0.02	Lancaster	6 [12]		<0.02	<0.02
2,6-dimethoxyphenol	0.03	Aldrich	570 [10]	0.09	36.1 ± 9.3	35.5 ± 7.3
4-vinylphenol	0.01	Lancaster	180 [13]	-0.13	85.7 ± 29.8	76.3 ± 14.0
4-allyl-2,6-dimethoxyphenol	0.01	Aldrich	1200 [6]	-0.35	7.7 ± 1.6	6.6 ± 0.7
vanillin	0.01	Aldrich	995 [12]	-0.41	22.8 ± 12.6	14.6 ± 4.7
acetovanillone	0.02	Aldrich	1000 [12]	-0.58	29.9 ± 2.6	26.5 ± 2.0
<b>LACTONES</b>						
<i>E</i> -whiskylactone	0.02	Aldrich	790 [2]	-0.24	24.1 ± 12.6	17.2 ± 9.6
<i>Z</i> -whiskylactone	0.01	Aldrich	67 [2]	-0.18	32.0 ± 17.4	23.4 ± 14.2
γ-nonalactone	0.01	Aldrich	25 [14]	-0.36	6.5 ± 1.8	4.8 ± 1.0
<b>γ-decalactone</b>	<b>0.07</b>	<b>Lancaster</b>	<b>10 [14]</b>	<b>0.91</b>	<b>23.7 ± 9.6</b>	<b>37.4 ± 5.7</b>
γ-butyrolactone	18	Aldrich	35000 [12]	0.04	6581 ± 271	6535 ± 303
<b>TERPENOLS</b>						
<b>linalool</b>	0.02	Aldrich	<b>25 [5]</b>	<b>-0.78</b>	<b>3.8 ± 0.9</b>	<b>3.1 ± 0.5</b>
α-terpineol	0.01	Fluka	250 [5]	-0.40	4.6 ± 0.6	4.4 ± 0.3
β-citronellol	0.15	Aldrich	100 [2]	0.00	<0.15	<0.15
geraniol	0.01	Fluka	20 [12]	0.00	<0.01	<0.01

compounds	LOD <sup>a</sup>	chemical standard	sensory threshold <sup>b</sup>	r	Right side	Left side
<b>VOLATILE SULPHUR COMPOUNDS</b>						
dimethyl sulphide (DMS)	0.53	Merk	25 [15]	0.19	11.49 ± 5.70	9.59 ± 0.54
hydrogen sulphide (H <sub>2</sub> S)	0.01	*	1.1-1.6 [16]	-0.28	1.10 ± 0.64	1.25 ± 0.48
<b>methanethiol (MeSH)</b>	<b>0.24</b>	<b>Fluka</b>	<b>1.8- 3.1 [17]</b>	<b>0.76</b>	<b>1.77 ± 0.57</b>	<b>2.97 ± 0.54</b>
ethanethiol (EtSH)	0.14	Sigma-Aldrich	1.1 [15]		<0.00014	<0.00014
<b>POLYFUNCTIONAL MERCAPTANS</b>						
2-methyl-3-furanthiol (MF)	**	**	0.004 [18]	-0.21	0.07 ± 0.02	0.06 ± 0.01
2-furfurylthiol (FT)	0.0002	Lancaster	0.0004 [19]	0.13	0.004 ± 0.002	0.005 ± 0.002
4-methyl-4-mercapto-2-pentanone (MP)	0.002	Alfa Aesar	0.0008 [20]	0.44	0.004 ± 0.001	0.004 ± 0.002
3-mercaptohexyl acetate (MHA)	0.0014	Oxford Chemicals	0.004 [20]	0.11	0.006 ± 0.009	0.017 ± 0.030
3-mercaptohexanol (MOH)	0.0066	Alfa Aesar	0.06 [20]	0.45	0.47 ± 0.20	0.59 ± 0.08
benzylmercaptane (BM)	0.0002	Fluka	0.0003 [21]	-0.38	0.002 ± 0.001	0.002 ± 0.000

<sup>a</sup>Limit of Detection (LOD) was calculated using  $3 S/m$  (S is the standard deviation of the response; m is the slope of the calibration curve).

<sup>b</sup>Odour thresholds. Reference in which the odour threshold value has been calculated is given in brackets. [1] Ferreira et al. (2002). [2] Etievant et al. (1991). [3] Guth (1997). [4] Escudero et al. (2004). [5] Ferreira et al. (2000). [6] Gemert (2003). [7] Aznar et al. (2003). [8] Peinado et al. (2004). [9] San Juan et al. (2012). [10] Lopez et al. (2002). [11] Ferreira et al. (2009). [12] Escudero et al. (2007). [13] Boidron et al. (1988). [14] Gemert (2003). [15] Gonial and Noble (1987). [16] Sibert et al. (2009). [17] Solomon et al. (2010). [18] Tominaga et al. (2006). [19] Tominaga et al. (2000). [20] Tominaga et al. (1998). [21] Tominaga et al. (2003) - These References are available in the supplementary material 3.

\*H<sub>2</sub>S was produced by addition of an Ar-bubbled water solution of Na<sub>2</sub>S (supplied by Sigma-Aldrich, St. Louis, MO, USA) at pH 9.6

\*\*concentration of MF expressed as micrograms per liter of furfurylthiol (FT)

**Table 3.** Average ( $\pm$  standard deviation) and significance (P) of variables significantly different ( $P < 0.05$ ) between wines of the left and right side of the river.

	<b>Left side</b>	<b>Right side</b>	<b>P</b>
Minerality score	3.3 $\pm$ 0.1	3.0 $\pm$ 0.2	0.016
MeSH vector (OAV) <sup>a</sup>	1.65 $\pm$ 0.30	1.00 $\pm$ 0.32	0.023
Norisoprenoid vector (OAV)	59.2 $\pm$ 1.93	69.4 $\pm$ 5.91	0.017
Copper (mg L <sup>-1</sup> )	0.19 $\pm$ 0.03	0.30 $\pm$ 0.06	0.027

<sup>a</sup>Expressed as OAVs, which corresponds to average concentrations of 3.0 $\pm$ 0.5  $\mu$ g L<sup>-1</sup> (left side) and 1.8 $\pm$ 0.6  $\mu$ g L<sup>-1</sup> (right side).

Figure 1

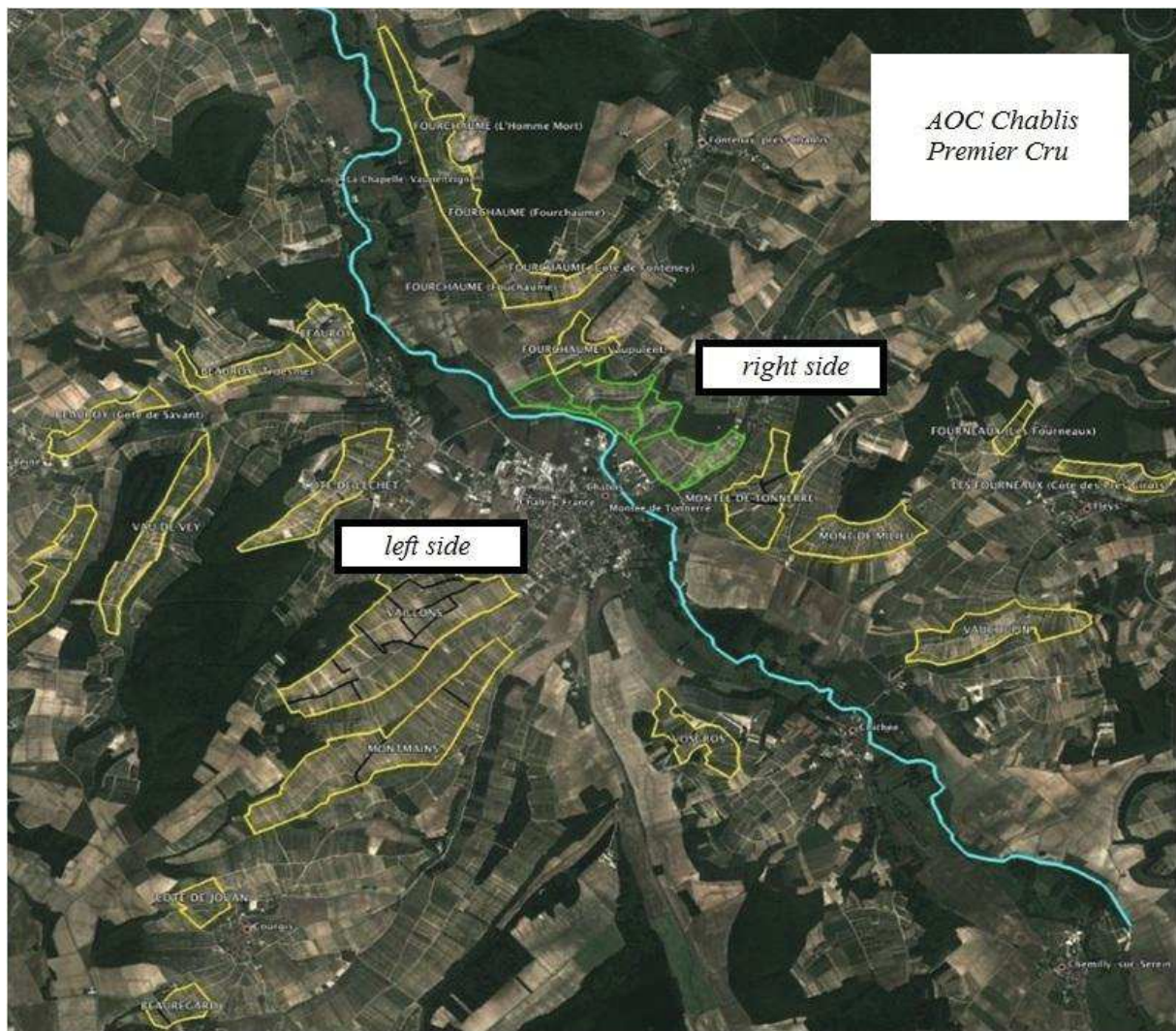
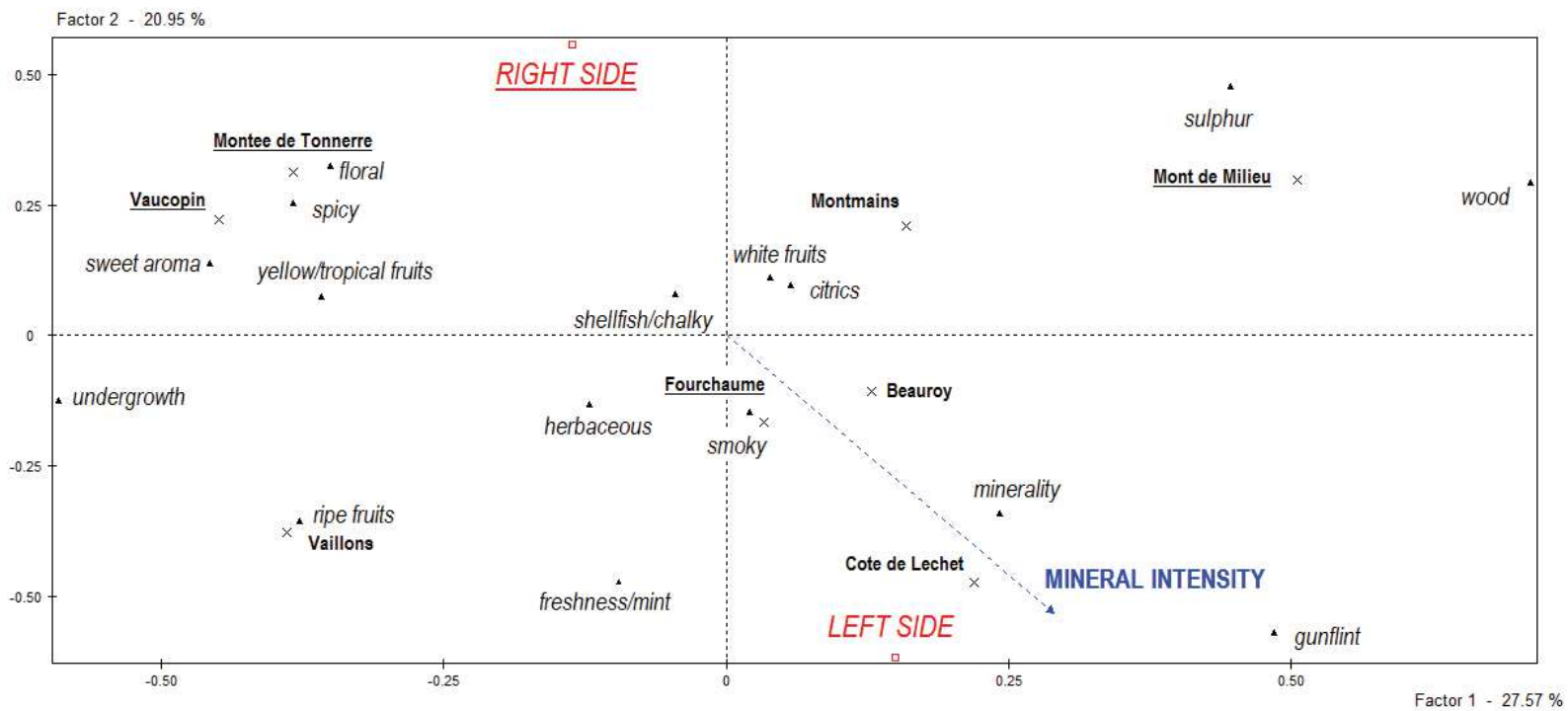
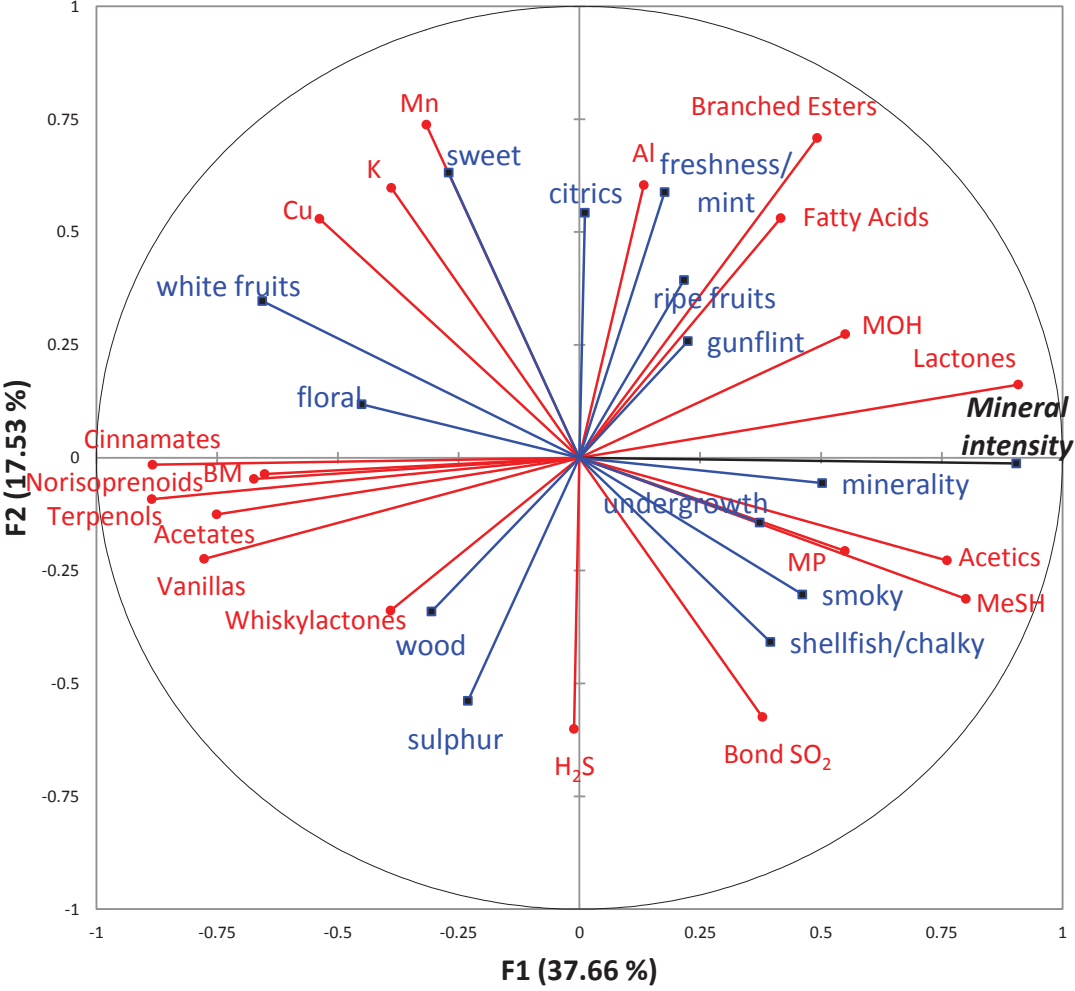


Figure 2

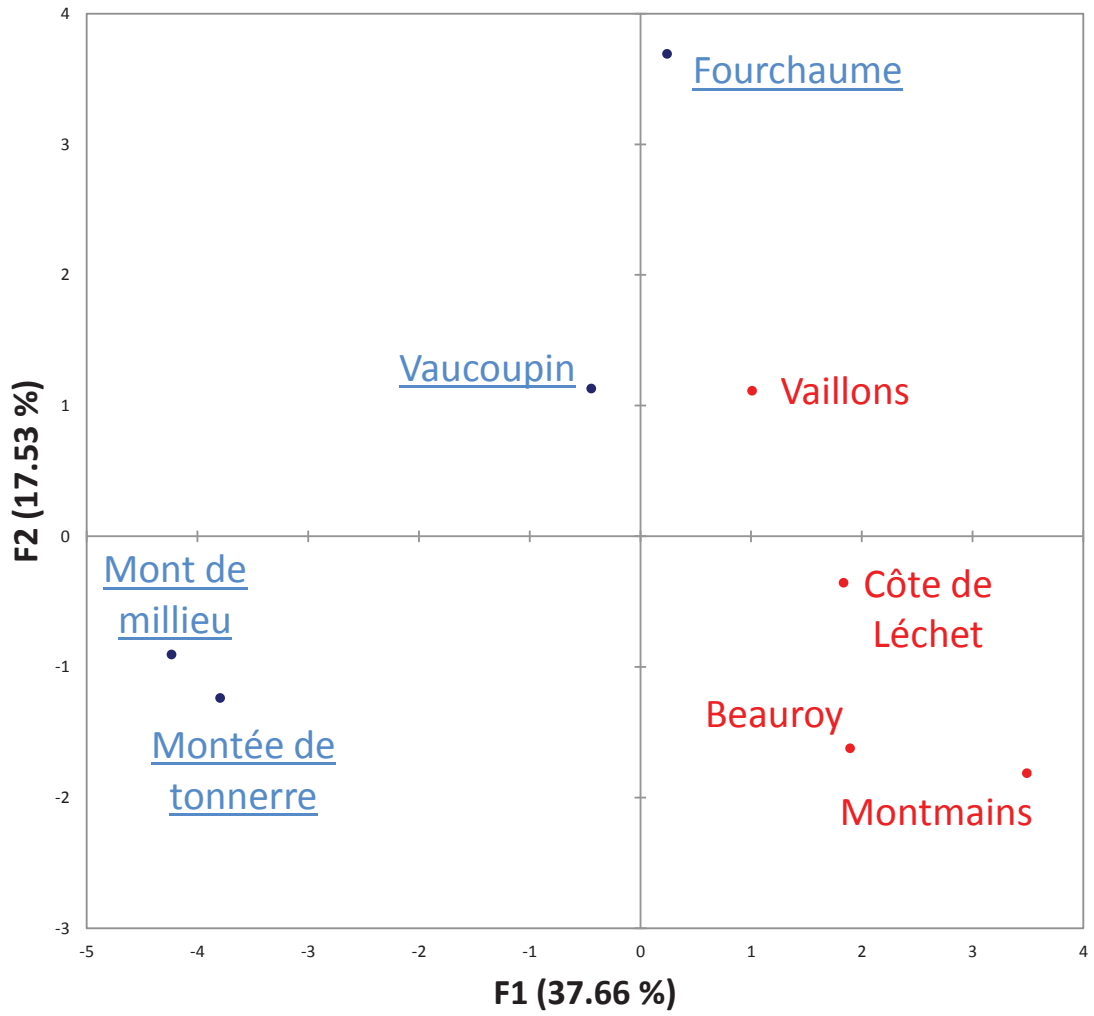


Figure(s)  
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a)



b)



**Supplementary Material**

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