

1     **Assessing concentration changes of odorant compounds in the thermal-mechanical drying**  
2                     **phase of sediment-like wastes from olive oil extraction**

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13    ***Abstract***

14    In the industrial production of olive oil, both solid wastes and those produced from their  
15    incineration are a serious environmental problem since only 20% w/w of the fruit becomes oil  
16    and the rest is waste, mainly orujo and alperujo. A key aspect to transform these wastes into an  
17    important source of energy such as pellets is to recognize the most appropriate time of the year  
18    for waste drying, with the objective of minimizing the environmental impact of the volatile  
19    compounds contained in the waste. In this work, the emissions produced during thermal-  
20    mechanical drying were studied along a period of six months of waste storage in which alperujo  
21    and orujo were stored in open containers under uncontrolled environmental conditions. The  
22    studied emissions were produced when both wastes were dried in a pilot rotary drying trommel  
23    at 450°C to reduce their initial humidity of around 70-80% w/w to 10-15% w/w. Results

24 indicated that when the storage time of the wastes in uncontrolled environments increases, the  
25 emission of odorant compounds during drying also increases as a consequence of the biological  
26 and chemical processes occurring in the containers during waste storage. The main odorant  
27 VOCs were quantified monthly for six months at the outlet of the drying trommel. It was  
28 determined that the drying of this type of waste can be carried out properly until the third month  
29 of storage. Afterwards, the concentration of most VOCs produced widely exceeded the odor  
30 thresholds of selected compounds.

31

### 32 ***Keywords***

33 Agroindustrial waste; alperujo and orujo; rotary dryer emissions; volatile organic  
34 compounds; biomass drying

### 35 ***Highlights***

- 36 - The high temperature in the drying trommel produces odorant VOCs
- 37 - VOCs increase their concentration in alperujo and orujo over time
- 38 - Degradation of organic matter is the cause of VOCs production in alperujo and orujo
- 39 - The calorific value of alperujo and orujo does not change over time
- 40 - Wastes must be dried within a period of 3 months after their production

41

### 42 ***1. Introduction***

43 Between 2016 and 2017, the production of olive oil reached a global amount of 2.9 million tons.  
44 The European Union occupied 62% of the production corresponding to 1.8 million tons. This  
45 production was concentrated in Spain, Italy and Greece [1]. Despite the fact that Chile only

46 represents 0.5% of the worldwide production, a progressive increase in recent years has been  
47 observed, especially by the incorporation of Chilean products in the national and international  
48 market in countries such as China, USA and Australia, reaching today about 1,700 million  
49 consumers. These figures have generated a sustained growth in the amount of land planted with  
50 olive trees in Chile, increasing by 32% compared to 2004 [2].

51  
52 Since 20% w/w of olive oil is obtained in the extraction process and about 80% w/w corresponds  
53 to waste, the sustained increment in the production has led to higher waste generation and to a  
54 significant increase of environmental impacts such as odor nuisance and contamination of  
55 groundwater [3]. Olive mill solid wastes are mainly alperujo and orujo. Alperujo is the residue  
56 obtained from the two-phase process, while orujo is the residue of the three-phase process. Both  
57 are an aqueous mixture rich in organic matter and other derivatives [4]. Studies conducted by  
58 Christoforou [5] describe olive-mill solid wastes as an important source of energy given that  
59 their calorific value is between 15.6 MJ kg<sup>-1</sup> to 19.8 MJ kg<sup>-1</sup> in dry basis. However, one of their  
60 disadvantages is the high moisture content, which lies between 60% w/w - 70% w/w,  
61 respectively [6,3] This implies that these residues should be dried before any further use to reach  
62 a moisture content of around 8% w/w in a dry basis. This process has been carried out for many  
63 years to obtain a product with added value, such as in the case of oils extracted with solvents [7].  
64 The most used systems for this purpose are rotary dryers [8]. Such drying systems produce  
65 evaporation of volatile organic compounds (VOCs) when the temperature in the chamber  
66 increases; they also produce condensable compounds and particle emissions as a consequence of  
67 volatilization, steam production and thermal destruction [7, 9]. Additionally, significant risks of

68 producing polycyclic aromatic hydrocarbons due to the adherence of the residues to the drum  
69 walls exist [8]. Emissions produced depend on waste composition, which varies over time during  
70 waste storage due to the effect of environmental variables (temperature, rainfall and humidity) on  
71 the chemical and biological processes occurring in the storage reservoirs [10]. In addition to the  
72 fact that emissions from thermal-mechanical drying of such waste have been poorly addressed in  
73 the literature, a significant variability of their composition is expected considering the influence  
74 of the storage time in the release of VOCs from open reservoirs. Such variability has not been  
75 addressed previously in literature to the authors' knowledge.

76  
77 Fagnäs et al. [9] determined that when drying temperatures are below 100 °C, monoterpenes  
78 and sesquiterpenes are produced during biomass drying. Conversely, when temperatures are  
79 above 100 °C, compounds such as fatty acids, resin acids and higher terpenes are produced,  
80 which are responsible for haze formation around these kinds of systems due to air cooling; which  
81 cause odor and visual discomfort. On the one hand, Fagnäs et al. [9] determined that other  
82 compounds released during drying processes are alcohols, organic acids and aldehydes, which  
83 are the product of thermal destruction of hemicellulosic materials when temperatures exceed 150  
84 °C. On the other hand, a study conducted by Jauhiainen et al. [11] evaluated gaseous emissions in  
85 the pyrolysis and combustion processes in a tubular laboratory batch reactor of olive oil solid  
86 waste at different temperatures from 750 to 1050 °C. This study showed that a great abundance  
87 of compounds is generated and that their concentrations and type of compounds increase along  
88 with temperature. The most abundant molecules found were methane, benzene, ethene, ethane,  
89 propane, propene, butane, butene, butadiene and toluene.

90

91 The aim of this work was to characterize and quantify the VOCs produced when the alperujo and  
92 orujo were dried using a pilot-scale rotary dryer (trommel). Both residues were stored outdoors  
93 and under uncontrolled environmental conditions for six months, simulating the actual industrial  
94 conditions, to evaluate the impact of the storage time on the dryer emissions. Thus, the initial  
95 humidity for each residue fluctuated between 50-80% w/w and was reduced to around 10–15%  
96 w/w in order to be suitable for pelletization.

97

## 98 **2. Materials and methods**

### 99 ***2.1. Identification of the samples***

100 In June 2017, six samples from two different mills were obtained, three for alperujo and three for  
101 orujo. Samples were taken from the Maule Region, Chile. Samples of orujo and alperujo were  
102 extracted from the oil mills from the only outlet duct of the waste and deposited in 200 L plastic  
103 containers. The procedure for sample extraction and the geographical location of the oil milling  
104 sites are described in Hernández et al. [10]. Each sample was identified and standardized to a  
105 mass of 200 kg and moved and stored under uncontrolled environmental conditions outdoors in  
106 the Curicó Campus, University of Talca, Curicó, Chile.

107

### 108 ***2.2. Environmental conditions***

109 Provided that the containers were located outdoors and in order to evaluate the effect of  
110 environmental conditions, a daily measurement for temperature, humidity, wind speed and  
111 amount of rainfall was carried out during the entire experimental period of six months, which

112 was averaged on a monthly basis (Table T1 in the supplementary material). These parameters  
113 were studied since relevant information can be obtained regarding the changes that can occur in  
114 the odorant compounds due to the exposure time and the climate variability related to the rainfall  
115 and the temperatures as the year progresses from winter to spring. In any case, the influence of  
116 the environmental conditions on the samples in the study herein reported was found to be similar  
117 to that already reported by Hernández et al. [10], which was performed for samples of the same  
118 type of wastes and exposed to environmental conditions in the same location but performed one  
119 year in advance to this current study.

120  
121 Representative samples were extracted every month for a six-month period from each container  
122 containing orujo and alperujo waste as described elsewhere [10]. Every month, subsamples from  
123 different parts of the container of each residue were mixed independently in a 50 L plastic  
124 container and manually stirred to obtain a final homogeneous sample. These mixtures of orujo  
125 and alperujo were separated every month as follows: 5.0 kg frozen at -18 °C stored as control  
126 samples; 1.0 kg for laboratory tests in triplicate, using standardized methods according to DIN  
127 [12] and AOAC INTERNATIONAL [13] and 15.0 kg of orujo and alperujo samples that were  
128 divided into three subsamples of 5.0 kg each to be dried in the drying trommel in triplicate. Table  
129 1 shows the main characteristics of the physical-chemical parameters analyzed of each waste  
130 prior to its drying phase.

131 **Table 1:** Results of the physical-chemical analysis for samples of alperujo and orujo  
132 corresponding to the initial conditions before processing in the drying trommel over time.  
133 Deviations correspond to the standard deviation of triplicates.

Month	Moisture content (% wb)**		Ashes (% wb)*		Measuring heating value (MJ kg <sup>-1</sup> )*	
	Oven method - AOAC 945.15		Muffle method – AOAC 940.26		Norm DIN Serie 51.900	
	Alperujo	Orujo	Alperujo	Orujo	Alperujo	Orujo
Jul	77.7±0.1	79.5±0.2	2.4±0.1	3.2±0.1	22.3±0.1	22.4±0.2
Aug	77.9±0.5	80.2±0.3	2.2±0.1	3.1±0.1	22.1±0.2	22.4±0.1
Sept	80.0±0.5	81.8±0.4	1.9±0.2	2.9±0.1	22.4±0.1	22.5±0.1
Oct	73.1±0.2	77.4±0.2	1.6±0.1	2.7±0.1	22.2±0.1	22.4±0.2
Nov	60.5±0.4	63.4±0.2	1.6±0.1	2.2±0.1	22.1±0.1	22.6±0.2
Dec	53.0±1.0	55.4±0.4	1.2±0.2	2.0±0.1	22.3±0.1	22.7±0.2

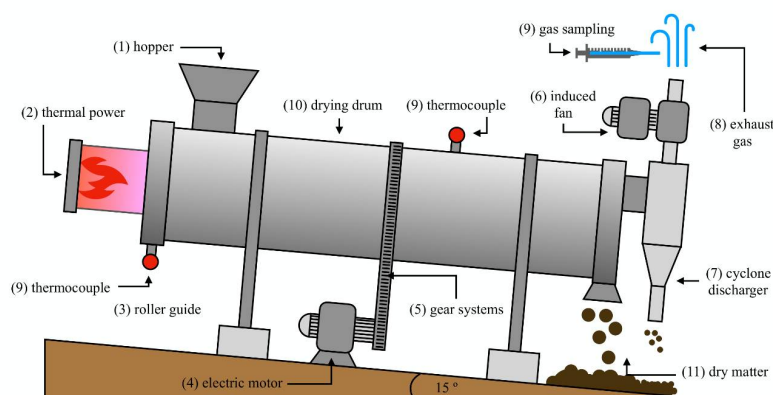
134 \*Dry basis; \*\*wet basis

135

136 Each month, orujo and alperujo samples were introduced in triplicate in a pilot-scale rotary  
 137 drying trommel shown in Figure 1. The drying trommel consisted mainly of a turbo-heater (2) of  
 138 propane-butane gas (model SG30) with a direct flame that provides the caloric energy to the  
 139 system. The entry feeding hopper (1) for the wet material (alperujo and orujo) had a height of 50  
 140 cm, the diameter in the upper part was 50 cm and the diameter in the lower part was 20 cm. The  
 141 concentric drum (10) had a length of 2500 cm and 80 cm in diameter. In addition, paddles were  
 142 built inside the drum to allow samples to be homogenized. Finally, the trommel had two orifices,  
 143 one for the exit of the dry biomass (11) and the other for the exit of the exhaust gases and  
 144 particulate matter (8). The exhaust gases and particulate matter passed through a separation  
 145 cyclone (7) to extract fine particles, while the hot gases were released through an outlet pipe  
 146 where gas samples were taken for Volatile Organic Compounds (VOCs) analysis.

147

148 **Figure 1:** Biomass drying trommel. (1) hopper; (2) thermal power; (3) roller guide; (4) motor;  
 149 (5) gear systems; (6) induced fan; (7) cyclone discharger; (8) exhaust gas; (9) thermocouple; (10)  
 150 drying drum; (11) dry biomass output.



151  
152 The working conditions of the drying trommel were selected based on those normally used in the  
153 olive oil production industry. A working temperature in the concentric drum of  $420 \pm 10$  °C was  
154 selected and controlled using two thermocouples (PT100), one for the entry of hot gases into the  
155 system and the other inside the drum of the drying trommel. The drum rotation speed of the  
156 system was programmed at 5.0 RPM and an inclination of  $15^\circ$  in order to achieve a better  
157 displacement of the material inside the drum and achieve a homogeneous drying in a total time  
158 of approximately 15 minutes. The final outlet moisture of the alperujo and orujo was between  
159 10-15% w/w on dry basis.

160  
161 For each sample of orujo and alperujo, three tests per sample were carried out allowing to  
162 evaluate the outlet emissions and waste characteristics after the drying process (Table T2,  
163 supplementary material). In all cases, the average humidity of the material after the tests  
164 fluctuated between 11-13% w/w on dry basis, while the average for ash content and the



165 measuring heating value were 1.5-3.0% w/w and 22.3 MJ kg<sup>-1</sup>, respectively, for both alperujo  
166 and orujo.

167 **Table T2:** Results of physicochemical analysis with standard deviation for samples of alperujo  
168 and orujo as exit conditions to the drying trommel in time.

Mom	Moisture content (% wb)** Oven method - AOAC 945.15)		Ashes (% wb)* Muffle method – AOAC 940.26		Measuring heating value (MJ kg <sup>-1</sup> )* Norm DIN Serie 51.900	
	Alperujo	Orujo	Alperujo	Orujo	Alperujo	Orujo
jul	12.2±0.1	12.4±0.1	2.2±0.1	3.1±0.1	22.4±0.1	22.5±0.1
aug	11.3±0.1	10.4±0.2	2.1±0.1	3.0±0.1	22.1±0.1	22.2±0.1
sept	12.5±0.1	11.4±0.1	2.0±0.1	2.8±0.1	22.5±0.1	22.1±0.1
oct	13.5±0.1	12.4±0.1	1.8±0.1	2.8±0.1	22.2±0.1	22.6±0.1
nov	12.4±0.1	12.7±0.1	1.7±0.1	2.5±0.1	22.6±0.1	22.9±0.1
dec	12.6±0.1	11.5±0.2	1.4±0.1	2.1±0.1	22.3±0.1	22.1±0.1

169 \*Dry base; \*\*wet base

170

#### 171 **2.4. Sampling of VOCs and conditions of thermal desorption gas chromatography mass** 172 **spectrometry (TD-GC/MS)**

173 At a distance of 50 cm from the outlet pipe of the exhaust gases of the drying trommel, three  
174 samples were taken for each test at different times (5 min, 10 min and 15 min) at an average  
175 outlet temperature of 150 °C. In order to extract the gas samples, a suction pump (Markes Easy  
176 VOC model LP-1200) was used, extracting an amount of 100 mL through an absorbent tube  
177 (Markez C2-BAXX-5315 odor/sulfur. C6/7-C30, thiols and mercaptans). Once the gases were  
178 adsorbed, VOCs desorption was carried out using a cold trap of thermal desorption (Markes  
179 model Unity-xr). The gases were extracted in Split mode, driven with helium for 1 min to the hot  
180 trap programmed at 300 °C. Then cooled to 20 °C in the cold trap to finally be heated to 300 °C  
181 for 5 min. VOCs were transferred by means of a transfer line heated at 200 °C to one column  
182 (Rtx-5MS w/integra-guard Crossbond 5 % diphenyl – 95 % dimethyl polysiloxane. 30 meter,

183 0.25 mmID, 0.25  $\mu\text{m}$  df) installed in a GC/MS (Thermo Fisher Scientific, model Trace 1300 /  
184 ISQELTL). The working conditions of the GC for the oven were in Split mode with a working  
185 temperature between 40  $^{\circ}\text{C}$  and 220  $^{\circ}\text{C}$ . Flow: 1.2 mL/min; Split Ratio: 10  $^{\circ}\text{C}/\text{min}$ , the transfer  
186 line temperature of the MS detector was 200  $^{\circ}\text{C}$  while the ion source temperature was set at 250  
187  $^{\circ}\text{C}$ . The qualitative identification of VOCs was carried out using the Chromeleon 7.2 software  
188 package, which is compatible with the NIST library [14], using retention times observed in the  
189 chromatograms.

190

### 191 **2.5. Reagents**

192 All the standards used for the quantification of VOC concentrations in the TD/GC-MS  
193 corresponded to substances with purities greater than 95%. Hexane, octane and nonane were  
194 purchased and prepared in methanol using a mix of 16 components, a calibration standard  
195 provided by Restek (ref. D3710-95). The other compounds were purchased individually from  
196 Merck, Sigma-Aldrich and Lancaster Synthesis, and were prepared as standard solutions in  
197 methanol.

198

### 199 **3. Results and discussion**

200 Among all the samples extracted from the exhaust gases during alperujo and orujo drying and  
201 later analyzed by TD-GC/MS, more than 600 compounds were identified. However, a large list  
202 of them only appeared a few times or in small abundances, well below their odor threshold. In  
203 addition, the reliability of some identified compounds was below 98% coincidence with the  
204 NIST library [14]. Thus, inventory of all the compounds found over time was reduced to these

205 shown in Table 2, in which VOCs were classified by families, including the months in which  
 206 each VOC was detected during the course of the study. Only those compounds that were found  
 207 in more than 25% of the 108 output samples were considered representative in terms of  
 208 emissions, following the criteria described by Dorado et al. [15] for compost maturation  
 209 emissions in a wastewater treatment plant.

210

211 **Table 2:** Selected VOCs detected during the drying process for alperujo and orujo samples.

Family	Name	Months (1-6)		Odor threshold ppm <sub>v</sub>	Reference
		alperujo	orujo		
Aldehydes	2-Furancarboxaldehyde, 5-methyl-	1, 3, 4	1	3.0	Sung et al.[16]
	3-Cyclopentene-1-acetaldehyde, 2-oxo-	1, 3	1- 3		
	9-Octadecenal	3, 4	-	>1.0	Caprino et al.[17]
	Benzaldehyde	1-6	1-6	0.35-3.5	Buttery et al.[18]
	Furfural	1-6	1-6	3.0-23.0	Buttery et al.[18]
	Hexanal	1-6	1-6	0.28	Nagata [19]
	Methyl glyoxal	3, 4	3- 5		
	Nonanal	1-6	-	0.34	Nagata[19]
	Octanal	1-6	-	0.01	Nagata[19]
Amides	Propanamide, 2-hydroxy-	2- 6	1-6		
Amines	1,4-Pentadiene	2-3	1-2		
	Pyridine, 3-ethyl-	2-3	2-3		
Alcohols	1-Dodecanol, 3,7,11-trimethyl-	-	1-3		
	2-Methoxy-4-vinylphenol	2-3	1-6	0.003	Nagata[19]
	3-tert-Butyl-4-hydroxyanisole	2-6	2-3		
	Phenol	1-6	1-6	0.0056	Nagata[19]
	Phenol, 2-methoxy-4-(1-propenyl)-	2-5	1-6		
	Phenol, 2,6-dimethoxy-	1-2	1		
	Phenol, 4-ethyl-2-methoxy-	1-5	1-6		
	1-Dodecanol, 3,7,11-trimethyl-	2-5	2-5		
	1-Hexadecanol, 2-methyl-	1	1-2		
	2-Furanmethanol	1-6	1-6	8.0	Montgomery[20]
Aromatic HCs	3-Nonen-1-ol, (E)-	-	2-3		
	5-tert-Butylpyrogallol	2-3	2-3		
	Benzene, 1-azido-3-methyl-	2-3	2		
Esters	Benzene, 1,3-dimethyl-	2-5	2		
	Toluene	1-6	1-6	0.33	Nagata[19]
	10-Octadecenoic acid, methyl ester	2-3	-		
Carboxylic acids	Hexanoic acid, 2-phenylethyl ester	2-6	-		
	Acetic acid	1-6	1-6	0.0060	Nagata[19]
	Propanoic acid	4-5	-	0.0057	Nagata [19]
	9-Hexadecenoic acid	1-6	-		

Aliphatic HCs	1-Decene	3-6	5-6	99.808	<a href="http://www.odourthreshold.com">http://www.odourthreshold.com</a> [21]
	2-Octene	-	4-5		
	8-Heptadecene	5	3-6		
	Heptane	-	1-6		
	Hexane	1-6	1-6	1.5	Nagata[19]
	Nonane	1-6	1-6	2.2	Nagata [19]
	Octane	1-6	1-6	1.7	Nagata[19]
	Tetradecane, 2,6,10-trimethyl-	3-6	1-6		
Ketones	1,2-Cyclopentanedione, 3-methyl-	5-3	2		
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1-6	4-5		
	2-Cyclopenten-1-one, 2-methyl-	3-6	1-6		
	2-Propanone, 1-(acetyloxy)-	4-5	1-6		
	2-Propanone, 1-hydroxy-	2-6	5		
Ethers	Octane, 1-methoxy-	1-2	6		

212

213 Table 2 shows that there are a significant number of compounds repeated over time for the  
 214 samples of orujo and alperujo. Abundance is shown as 1-6, indicating that these compounds  
 215 appeared in all the sampling events throughout the 6 months of experimentation, while those that  
 216 appeared as a single number, for example 1, are those that only appeared in the first month  
 217 (June) of experimentation. The compounds found more frequently (all months from 1 to 6) in  
 218 both orujo and alperujo corresponded mainly to aldehydes (benzaldehyde, furfural and nonanal),  
 219 alcohols (phenol, 2-furanmethanol), carboxylic acids (acetic acid) and hydrocarbons (toluene,  
 220 hexane, octane and nonane). This lead to consider such molecules as target compounds for  
 221 further treatment of emissions from the drying process. Consequently, these compounds were  
 222 later selected for further quantification. Interestingly, Fagernäs et al. [9] showed that these types  
 223 of molecules appear mostly when the temperature exceeds 150 °C because the process of thermal  
 224 destruction of the wood hemicellulose begins. In addition, Dalai et al. [22] demonstrated that  
 225 when the temperature in the rotary drying system increased from 60 °C to 250 °C in a time of 45  
 226 min for the drying of alfalfa, the presence of VOCs increased, especially hydrocarbons, alcohols,  
 227 aldehydes and ketones. Thus, emissions are increased when the temperature in the drying system

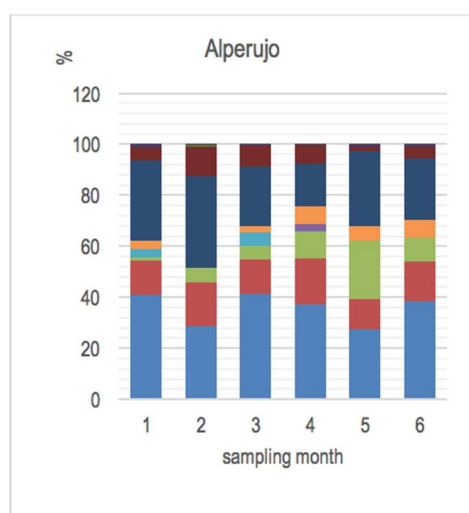
228 is increased, consequently increasing their environmental impact. Results were in agreement  
229 with those found by Jauhiainen et al. [11], in which the emissions produced in the combustion of  
230 olive oil solid waste were mainly hydrocarbons, such as ethane, propane, hexane, toluene,  
231 benzene as well as pyridinic derivatives and polycyclic aromatic hydrocarbons. This  
232 demonstrates that the most frequent molecules in Table 2 were representative of the emissions  
233 during the thermal-mechanical drying of these wastes. It is worth mentioning that a limited  
234 number of references were found regarding the odor threshold concentration for the compounds  
235 emitted from alperujo and orujo drying, highlighting that further research is needed to complete  
236 such gap. Fortunately, odor thresholds of those compounds found as representative of alperujo  
237 and orujo emissions during waste drying have been previously reported (Table 2).

238 In addition to the factors that influenced the drying process, VOCs found in the exhaust gases  
239 were also related to the prior storage stage as reported previously. Firstly, Hernández et al. [3]  
240 and Rodríguez et al. [23] showed that there are still a number of important oils (4.0% and 5.7%)  
241 in olive oil solid waste prior to drying. Secondly, Morales et al. [24] demonstrated that the main  
242 VOCs released from sour olive oils were hexanal, octane and acetic acid among other odorant  
243 compounds, which were identified as responsible for unpleasant odors when they exceeded their  
244 odor threshold concentration. Additionally, Hernández et al.[10] found that alperujo and orujo  
245 wastes generate VOCs, especially families of aldehydes and carboxylic acids when they are  
246 stored in open reservoirs in uncontrolled spaces. Moreover, the emissions' composition was  
247 influenced by the storage time and the environmental conditions.

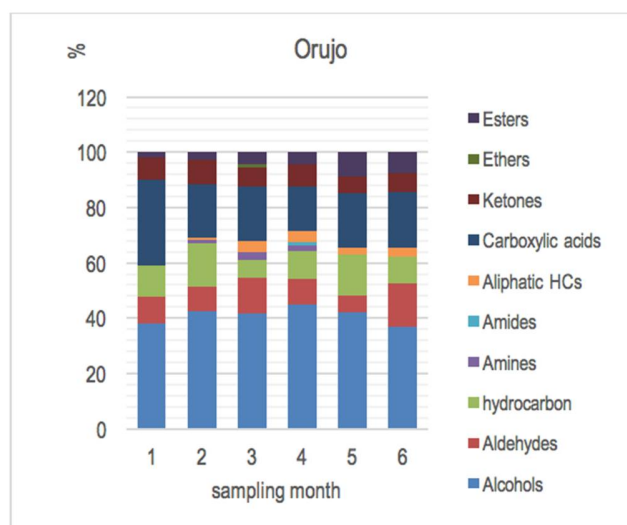
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249 Figure 2 shows the distribution over time of the VOCs families considered in Table 2 throughout  
250 the six months of study. Alcohols, carboxylic acids and aldehydes were those families that  
251 presented the highest percentage of compounds corresponding to an average of 36%, 27% and  
252 15%, respectively, for alperujo; and 41%, 21% and 10%, respectively, for orujo. In a previous  
253 study, Hernández et al. [10] determined that alcohols, carboxylic acids and aldehydes were also  
254 the predominant compounds in the emissions both from orujo and alperujo stored in open  
255 reservoirs due to a progressive decrease in the concentration of fatty acid methyl esters and  
256 alkenes in the emissions generated by biological and physical-chemical processes. Despite that  
257 most of the families showed no clear variability along the monitored period, still some families  
258 of VOCs showed a trend towards an increase or decrease over time. An increasing trend was  
259 observed for aliphatic and aromatic HCs in alperujo (Figure 2a) and for esters in orujo (Figure  
260 2b).

261 **Figure 2:** Percentage distribution of VOCs by family in alperujo and orujo in the six-month  
262 experimentation period.



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264

265

266 When results are analyzed based on the humidity of the samples (Table 1) and the rain  
 267 precipitations (Table T1, supplementary material), there were no significant changes in the  
 268 abundance of VOCs families for the waste drying process. The endothermic drying of waste has  
 269 the purpose of stabilizing the waste, reducing its weight and its volume, the latter as a  
 270 consequence of water loss by evaporation by the addition of heat. In addition, Castells et al. [25]  
 271 have shown that water when evaporated transports most of the VOCs, which are released to the  
 272 atmosphere.

273 **Table T1:** Average monthly weather conditions (www.wolframalpha)

		1	2	3	4	5	6
Weather conditions	Units	jul	aug	sep	oct	nov	dec
Precipitation (PPT)	mm	152	161	70	48	13	5
Min temperature (Tmin)	°C	-2	0	1	3	6	10
Max. temperature (Tmax)	°C	16	20	26	26	30	33
Wind speed (wind)	km h <sup>-1</sup>	19	18	13	19	15	14
Relative humidity (RH)	%	77	68	64	65	60	57

274

275

276 Dexter et al. [26] described that VOCs have a wide range of evaporation temperatures. Most of  
 277 them are evaporated at lower temperatures than water and their vaporization enthalpies are of the  
 278 order of magnitude of water. Therefore, when water and VOCs are released from the waste in the  
 279 form of vapor and contained within the mass of air circulating through the drying trommel, they  
 280 are removed from the system by means of depleting varying portions of the air mass charged  
 281 with steam through the discharge and replacement of this exhaust air with equivalent amounts of  
 282 fresh air containing less humidity. Tables 3 and 4 show the normal boiling temperatures of each  
 283 of the key odorant compounds found, which are lower than the operating temperature in the  
 284 dryer.

285  
 286 In addition, Table 3 and 4 show the quantification of VOCs that were considered as target  
 287 compounds according to the results in Table 1. Concentrations were compared with the odor  
 288 threshold concentrations also reported in Table 1.

289  
 290 **Table 3:** Normal boiling temperature and concentration of target VOCs in ppm<sub>v</sub> in exhaust gases  
 291 during alperujo drying

Family	Name	Boiling T °C	Jul	Aug	Sep	Oct	Nov	Dec			average
			1	2	3	4	5	6	min	max	
Alcohols	2-Furanmethanol	170.10*	3.0±0.1	3.1±0.1	3.5±0.1	4.0±0.1	4.2±0.1	5.2±0.2	3.0	5.2	3.8±0.5
	Phenol	181.93*	0.1±0.1	0.2±0.1	0.3±0.1	0.4±0.1	0.9±0.2	1.0±0.1	0.1	1.0	0.5±0.4
Aldehydes	Benzaldehyde	178.66*	3.5±0.0	4.0±0.1	4.2±0.1	4.8±0.2	4.9±0.1	5.1±0.1	3.5	5.1	4.4±0.6
	Furfural	161.55**	6.3±0.1	7.5±0.1	7.8±0.1	8.3±0.1	8.9±0.0	10.5±0.0	6.3	10.5	8.2±1.4
	Hexanal	128.14*	0.1±0.1	0.5±0.0	0.8±0.0	1.2±0.0	1.3±0.1	1.5±0.0	0.1	1.5	0.9±0.5
	Nonanal	194.93*	0.3±0.0	0.6±0.1	0.9±0.1	1.5±0.0	1.8±0.1	2.1±0.0	0.3	2.1	1.2±0.7
	Octanal	174.20*	0.1±0.0	0.1±0.1	0.5±0.1	0.9±0.0	1.1±0.2	1.2±0.1	0.1	1.2	0.7±0.5
Aromatic HCs	Toluene	110.68*	0.5±0.1	0.7±0.2	0.7±0.1	0.8±0.1	0.9±0.1	1.2±0.1	0.5	1.2	0.8±0.2
Carboxylic	Acetic acid	118.01*	2.8±0.1	3.5±0.1	2.9±0.1	3.5±0.1	4.2±0.0	4.9±0.1	2.8	4.9	3.6±0.8



acids											
Aliphatic HCs	Hexane	68.73*	0.9±0.0	1.9±0.1	2.9±0.1	2.8±0.0	2.5±0.1	1.5±0.2	0.9	2.9	2.1±0.8
	Nonane	150.66*	2.1±0.1	2.9±0.1	3.0±0.1	1.5±0.1	1.9±0.1	2.0±0.1	1.5	3.0	2.2±0.6
	Octane	125.69*	3.2±0.0	3.2±0.1	3.5±0.2	2.1±0.0	1.0±0.1	0.5±0.1	0.5	3.5	2.3±1.3

292 \* DIPPR [27]

293 \*\* NIST [14]

294

295 **Table 4:** Normal boiling temperature and concentration of target VOCs in ppm<sub>v</sub> in exhaust gases

296 during orujo drying

Family	Name	Boiling T °C	Jul	Aug	Sep	Oct	Nov	Dec	mi max		average
			1	2	3	4	5	6	n		
Alcohols	2-Furanmethanol	170.10*	3.1±0.1	3.9±0.2	4.2±0.2	4.2±0.1	4.9±0.0	5.7±0.2	3.1	5.7	4.3±0.9
	Phenol	181.93*	0.1±0.1	0.1±0.1	0.8±0.2	0.7±0.1	1.2±0.1	1.8±0.2	0.1	1.8	0.8±0.7
Aldehydes	Benzaldehyde	178.66*	3.1±0.2	3.2±0.1	3.8±0.1	4.3±0.1	4.9±0.0	4.9±0.1	3.1	4.9	4.0±0.8
	Furfural	161.55**	3.9±0.1	4.3±0.1	5.8±0.1	5.5±0.2	6.9±0.1	8.6±0.0	3.9	8.6	5.8±1.7
	Hexanal	128.14*	1.7±0.0	1.1±0.1	1.3±0.1	2.1±0.2	2.2±0.1	2.3±0.0	1.1	2.3	1.8±0.5
	Nonanal	194.93*	0.2±0.0	0.5±0.0	0.9±0.1	0.9±0.1	1.1±0.0	1.5±0.0	0.2	1.5	0.9±0.5
	Octanal	174.20*	0.2±0.1	0.2±0.0	0.8±0.1	1.2±0.2	1.8±0.2	2.1±0.1	0.2	2.1	1.1±0.8
Aromatic HCs	Toluene	110.68*	0.8±0.1	0.8±0.2	1.2±0.2	1.3±0.1	1.7±0.2	2.1±0.1	0.8	2.1	1.3±0.5
Carboxylic acids	Acetic acid	118.01*	2.4±0.1	3.2±0.1	3.8±0.1	4.1±0.0	4.5±0.1	5.2±0.1	2.4	5.2	3.9±1.0
Aliphatic HCs	Hexane	68.73*	2.1±0.1	2.0±0.1	2.1±0.2	1.9±0.1	1.2±0.0	1.0±0.2	1.0	2.1	1.7±0.5
	Nonane	150.66*	2.4±0.1	3.1±0.1	3.4±0.1	3.8±0.0	4.2±0.1	4.1±0.1	2.4	4.2	3.5±0.7
	Octane	125.69*	1.2±0.1	2.1±0.1	2.2±0.3	1.9±0.1	0.5±0.2	0.2±0.0	0.2	2.2	1.4±0.9

297 \* DIPPR [27]

298 \*\* NIST [14]

299

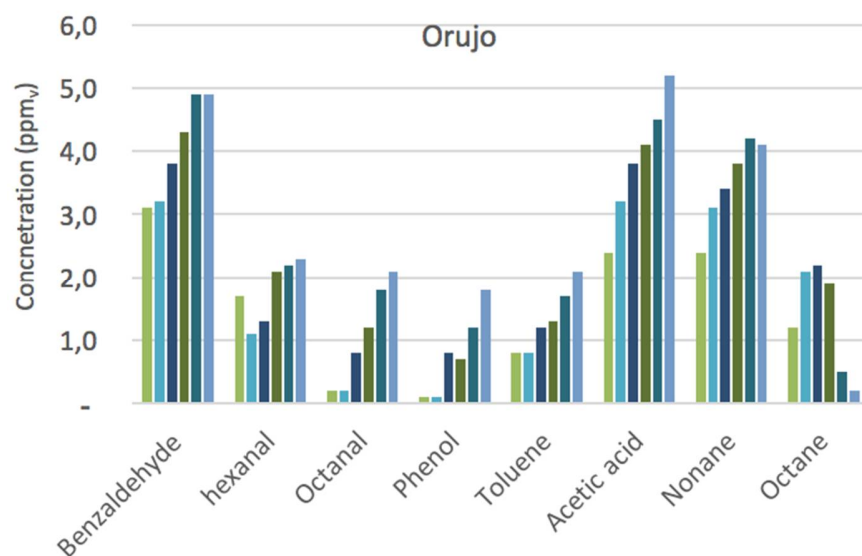
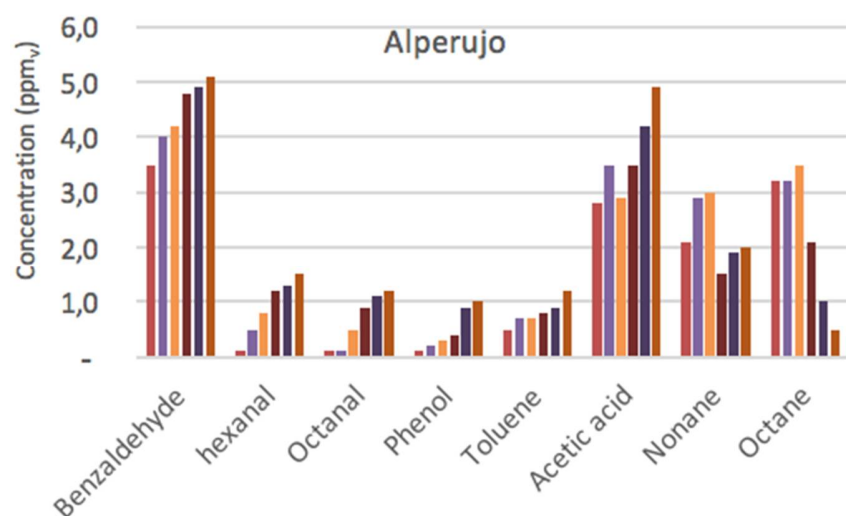
300 Except for furfural and 2-furanmethanol, concentrations of all target compounds exceeded their  
 301 odor threshold in all samples analyzed in both alperujo and orujo. A comparison of the odor  
 302 thresholds in Table 1 with the concentrations of odorants in Table 3 and 4 show that for alperujo  
 303 and orujo, the average benzaldehyde concentration exceeded by 25.7 % and a 14.3 %, respectively,  
 304 its odor threshold. Similarly, acid acetic exceeded by 81,666% and 86,666% their

305 odor threshold in alperujo and orujo, respectively. Hexanal, nonanal, octanal, phenol, hexane and  
306 toluene concentrations exceeded by 221%, 253 %, 6,900 %, 9,900 %, 40 % and 142 % their odor  
307 thresholds in alperujo and 543 %, 165 %, 10,900 %, 15,900 %, 13.3 % and 294 % their odor  
308 thresholds in orujo, respectively. Considering that most of the compounds reported in Tables 3  
309 and 4 are odorants that produce unpleasant odors when they are emitted to the environment [24],  
310 in practice, emissions from exhaust gases from oil mill waste drying need further treatment  
311 before their discharge to the environment to avoid bothersome impact on the surrounding areas  
312 of the industrial facilities

313  
314 Figure 3 graphically shows the variability of odorant concentrations quantified over time. This  
315 tendency to increase or decrease can be directly associated with the physical-chemical and  
316 biological changes that occurred in the samples over time given their organic composition and  
317 environmental conditions such as temperature and humidity, registered in Table 1. Hernández et  
318 al. [10] describes that the alperujo and orujo, when stored under uncontrolled environmental  
319 conditions over time, generate VOCs that increase their concentration as a result of the chemical  
320 and biological transformations that occur in these residues.

321

322 **Figure 3:** Monthly concentration of target VOCs found in alperujo and orujo drying emissions.



325 Aldehydes, in particular hexanal and octanal, increased their concentration over time for both  
 326 orujo and alperujo as a direct influence of oxidative processes product of the decomposition  
 327 reactions of the hydroperoxides formed by the slow self-oxidation of oleic acid as well as the  
 328 self-oxidation of lipoxygenase through the formation of hydroperoxide precursors 13-LOOH  
 329 (linoleic acid hydroperoxide).[28,29].

330

331 Interestingly, octane was the only VOC that showed a decreasing trend both in orujo and  
332 alperujo. Kalua et al. [29] described that this compound is recognized as a marker of oxidation in  
333 oils since it appears in high concentrations at the beginning of the process. In addition, Vichi et  
334 al. [28] indicated that octane is formed from hydroperoxide precursors 10-OOOH (oleic acid  
335 hydroperoxide) [28]. Thus, octane degradation can be a consequence of oxidative deterioration  
336 of oleic acid over time as described by Morales et al. [30]. In a 33-hour experiment, it was  
337 observed that the main volatile decomposition products found in oxidized olive oils were  
338 produced from monohydroperoxides of oleic, linoleic and linolenic unsaturated fatty acids that  
339 decreased their concentration over time, that is, in 98.2% at 0 h, 80.8% at 21 h and then 49.2% at  
340 33 h. Considering that the odorants are emitted from open reservoirs during waste storage and  
341 that initial humidity of wastes is almost constant during the 3-4 months (Table 1), results indicate  
342 that a proper alternative to reduce the impact of exhaust gases from the oil mill waste drying  
343 from an emissions perspective is to process them as soon as they are produced to minimize the  
344 overall emission of odorants from the storage and drying.

345  
346 Odor concentration measured in the gaseous emissions of a treatment process can be  
347 complemented with the individual odor impact values, which can help in the identification of the  
348 major odor contributors found in a complex odorous gas mixture. Table 5 shows the OIV per  
349 each VOC, which is obtained by dividing the average concentrations of each VOC quantified by  
350 its odor threshold according to literature data (Table 3).

351

352 **Table 5:** Odor impact value (OIV) for the individual VOCs based on average samples of orujo  
 353 and alperujo over time.

VOC Family	Compound	Odor Impact Value	
		alperujo	orujo
Alcohol	2-Furanmethanol	0.48	0.54
Aldehyde	Benzaldehyde	1.26	1.14
	Furfural	0.36	0.25
	Hexanal	3.21	6.43
	Nonanal	3.53	2.65
	Octanal	70.00	110.00
Aromatic	Phenol	89.29	142.86
	Toluene	2.42	3.94
	Acetic acid	3.60	3.90
Aliphatic HC	Hexane	1.40	1.13
	Nonane	1.00	1.59
	Octane	1.35	0.82

361

362 Results show that aldehydes and aromatic compounds, mainly phenol and octanal, are the ones  
 363 that present the highest odor impact value (OIV), implying that these families of compounds are  
 364 the precursors of the odors when the orujo and alperujo are dried in the drying trommel over  
 365 time. A study conducted by Morales et al. [24], shows that the high concentrations of aldehydes  
 366 in olive oils (rancid, fusty, winey-vinegary mustiness-humidity) are mainly produced by the  
 367 oxidation of unsaturated fatty acids, while the presence of acids that appear in the final part of  
 368 the oxidative process are the product of the oxidation of the previously formed aldehydes. In  
 369 terms of emissions, results of the impact reduction from thermal-mechanical drying of orujo and  
 370 alperujo point out that the development of treatment methods targeting particularly octanal,  
 371 hexanal and phenol may be much more efficient in reducing bothersome impacts than common  
 372 methods such as chemical scrubbers. Despite that further testing is warranted, such poorly

373 soluble compounds emitted at high temperatures could probably be adsorbed efficiently in  
374 activated carbon beds.

375

#### 376 **4. Concluding remarks**

377 This work was devoted to show the emissions of VOCs from samples of orujo and alperujo when  
378 they are stored over time and dried in a drying trommel. Results revealed that different odorant  
379 VOCs at varying concentrations are generated over time, which are often emitted directly into  
380 the environment through a chimney. As a consequence, bothersome impacts in the surrounding  
381 vicinities will be generated. These compounds corresponded mainly to alcohols, aldehydes,  
382 aromatics, carboxylic acid and hydrocarbons, which were found in concentrations higher than  
383 their odor threshold. Results showed that from the third month onwards, the concentrations of  
384 VOCs classified as odorants were intensified. Thus, when alperujo and orujo wastes are stored  
385 over time and subjected to various environmental changes, there are ideal times to carry out the  
386 drying process without generating major consequences of odorant compounds both in the drying  
387 phase and storage phase, implying that the shorter the time the less environmental consequences  
388 are generated.

389

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395

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