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VOCs and PM listing of *Eucalyptus globulus* combustion in residential wood stoves

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2223 ABSTRACT

24 Pollutant residential emissions from wood stoves have significant impacts both on the 25 environment and people's health. The above makes it essential to know the types of volatile 26 organic compounds emitted during combustion and explore their relationship with particulate 27 matter and greenhouse gas emissions. This paper studies and analyzes these emissions using 28 *Eucalyptus globulus* as fuel varying its moisture levels. Emissions were determined using an 29 adapted commercial stove. The concentration levels of volatile organic compounds and particulate matter increase with the moisture of wood. When analyzing volatile organic 30 compounds, particulate matter, and O₂ with the combustion stages of wood, it is found that 31 32 their concentrations were higher in the ignition and the reload stage. The concentrations of 33 CO_2 and NO_x were higher in the reload stage. Other chemical compounds, such as toluene, 34 xylene, and benzene, were also found within the volatile organic compounds listing, which 35 increased their concentration in the ignition and stable reload stages. However, in the 36 quenching stage, they are not present. Finally, the dispersion of these molecules in the environment is evaluated, obtaining that if the atmospheric conditions are adverse, these 37 38 molecules remain in the environment in direct contact with the people living in those places. Keywords: Biomass combustion, boiler load, particulate matter, volatile organic 39 40 compounds, volatile organic compounds emission, wood stove,

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43 **1. INTRODUCTION**

44 In the history of humankind, residential heating has been a basic need to maintain adequate 45 thermal comfort inside the homes. Different systems have been developed for this need, but 46 with great energy and environmental cost. Currently, wood is one of the cheapest and easily accessible methods to produce this energy, which is a source of heat for approximately 40%47 48 of the world's population (Sáenz-Ceja et al. 2017, Food and Agricultural Organization 2017). Besides, 80 % of wood comes from forest wood products (Berrueta et al. 2017). The wood 49 50 comes from different species: in urban areas, 95 % of wood corresponds to exotic species (50 51 % Eucalyptus globulus, 37 % fruit trees, and 8 % others), 4 % to waste wood and only 1 % 52 to native wood, while, in the rural sector, 90 % of wood corresponds to exotic species (35 % fruit trees, 33 % Eucalyptus globulus and 22 % others), 3 % to waste wood and 7 % to native 53 54 wood (Reyes et al. 2020a).

Chile is one of the pioneers in this use of *Eucalyptus globulus* for combustion, with an 55 available planted area of 860317 hectares (Molina-Mercader et al. 2019). In the process of 56 wood combustion in stoves, a variety of pollutants are produced such as volatile organic 57 58 compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), particulate matter (PM), 59 carbon monoxide (CO), carbon dioxide (CO₂) and NO_x (Vicente et al. 2020, Guerrero et al. 60 2019, Weinstein et al. 2020, Naeher et al. 2007, Bruce et al. 2000). These gases are released 61 into the environment and remain dispersed based on existing climatic conditions. In areas 62 with valley topography, temperature inversions at night limit the dispersion of pollutants 63 from sources of terrestrial origin (Allen et al. 2011). At night, atmospheric stability varies 64 from neutral to moderately stable, with an ambient temperature gradient smaller than the adiabatic dry temperature gradient (De Nevers 1998, Haro et al. 2018). This situation 65

generates that these VOCs. Other gases and PM are located at a lower altitude, producingdirect contact with the communities living in those places.

68 Different studies have referenced the effects on people's health due to wood combustion, 69 where acute upper respiratory tract infection, reduced lung function, and cough, among 70 others, are the most frequently reported (Aliyu et al. 2015, Basagaña et al. 2015, Satsangi et 71 al. 2014). Additionally, Naeher (2007) describes that there are about 200 types of VOCs in 72 wood combustion known as Hazardous Air Pollutants, where many of these are of particular 73 interest due to their carcinogenic effect (Grineski et al. 2016, Wu et al. 2009). Within this 74 group are benzo[a]pyrene, benzene, toluene, xylene, and ethylbenzene, which even in very 75 low concentrations produce severe effects on people ((International Agency for Research on 76 Cancer 2015, Bede-Ojimadu and Orisakwe 2020, Languille et al. 2020).

However, these studies do not incorporate the specific combustion of *Eucalyptus globulus*,
the main source of wood in Chile and other countries in Latin America and Oceania.

This work aims to study VOCs, PM, CO, NO_x and CO₂ produced in the combustion of 79 80 *Eucalyptus globulus*, considering different percentages of moisture and combustion stages 81 (ignition of Cycle 1, stable reload of Cycle 3, and quenching of Cycle 3), to quantify the degree of contamination that occurs when the wood is not treated and is not subjected to a 82 drying process before combustion. Price-Allison et al. (2019) reports that the higher the 83 84 percentage of relative humidity in wood, the more gases are produced in wood combustion, 85 indicating that moisture can be a key factor in these phenomena. The above affecting the 86 listing of VOCs and PM emissions of wood, differing from those already reported for other 87 types of wood since the type of wood is one of the factors that most affect emissions (McDonald et al. 2000). 88

89 2. MATERIALS AND METHODS

90 2.1. Experimental design

91 The tests were carried out in the laboratory of emissions of Kipus Technology Center at 92 Universidad de Talca, using a single-room wood stove from the Chilean manufacturer 93 Amesti, model Scantek 360. The stove has a nominal heat output of 8,5 kW and, according 94 to the manufacturer, an efficiency of 70 %. The stove operates with a natural draft, and it has 95 a staged air supply with primary and secondary air entries. The secondary air source can be 96 controlled manually via air damper. The stove tests were carried out 3 samples of with 30 cm 97 length of *Eucalyptus globulus* wood, the typical wood used in Chile for residential heating. 98 Three experiments were run using different relative humidity of wood: 1 sample dry wood 99 (9%), 1 sample wet wood (25%), and 1 sample extra-wet wood (33%). Three burn cycles were carried out per experiment to measure total PM emissions, combustion gases, and VOCs 100 101 in different combustion stages (ignition, reload and quenching phases). Gaseous exhaust gas 102 components were measured continuously (CO₂, CO, O₂, NO, NO₂). PM was measured with 103 single batch samples and VOCs were sampled in batch measurements by duplicate samples. 104 For each combustion cycle, the mass of wood logs added to the combustion chamber was calculated based on the nominal heat output of the stove (1,7 kg of dry wood logs; 2,1 kg of 105 106 wet wood logs; 2,4 kg of extra-wet wood logs), using the method reported by the Chilean 107 Superintendence of Energy and Fuels (SEC, 2020).

108 The PM emission was measured using Wöhler SM500, which uses a gravimetric method 109 with a sampling of 15 minutes. This PM analyzer was designed to comply with the European 110 standards defined in the First Ordinance on the Implementation of the Federal Immission 111 Control Act (Ordinance on Small and Medium-Sized Firing Installations) "1.BImSchV" 112 (Bundes-Immissionsschutzgesetzes). The first PM measurement was taken in the first cycle, 113 which is the ignition stages, starting the sampling immediately after closing the stove. The 114 second measurement was taken in the reload of the third cycle, immediately after closing the 115 stove. Finally, the third measurement was taken in the final stable stage of the third cycle, 45 116 minutes after closing the door. The samples for VOCs detection were taken by duplicate at 117 the same time when the PM sampling began. Table 1 shows the measurement technology and ogy. 118 the corresponding measurement accuracy used on the test setup.

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Table 1	:	Measurement	technology
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Device	Principle	Components	Range	Accuracy
Wöhler SM	Gravimetric	PM	$0,0 - 1000 \text{ mg/m}^3$	± 0,3 mg
500	Electrochemical	O ₂	0,0 – 21,0 vol%	± 0,3 vol%
	sensor	\cap		
	Electrochemical	CO	0,0 – 100000,0	± 100,0 ppm
	sensor		ppm	
Testo 350 XL	Electrochemical	NO	0,0 - 99 ,0 ppm	± 5,0 ppm
	sensor			
	Electrochemical	NO ₂	0,0 - 99,9 ppm	± 5,0 ppm
	sensor			
	Infrared sensor	CO_2	0,0 - 50 ,0 vol%	± 0,3 vol%
Minipo	Electrical	Relative	5,0-40,0 %	± 1,0 %
MWD-14A	resistance	humidity		

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124 The experimental setup is shown in Figure 1. The sampling point for combustion gases was 125 located at 1,9 m height over the stove. Additionally, the PM sampling was located at 3,0 m 126 over the stove, and the VOCs samples at 10,0 cm over the exit of gases at the top of the duct 127 4,0 m over the stove.



- Figure 1: Scheme for taking samples and images of the system used during the experiments.
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132 **2.2.** Conditions of Thermal Desorption-Gas Chromatography/Mass Spectrometry

133 (**TD-GC/MS**).

VOCs samples of 100 mL were taken by duplicate at a temperature of approximately 30 °C
using a hand vacuum pump (Markes Easy VOCs model LP-1200, Germany) and stored in
glass thermal desorption tubes (Markes C2-BAXX-5315 odor/sulfur. C6/7-C30, thiols and
mercaptans, Germany). The tubes were transported using a hermetic chamber (Markes model
Unity-xr, Germany).

The gases were extracted in Split mode, driven with helium for 1 min to the hot trap 139 140 programmed at 300 °C and then cooled to 20 °C in the cold trap to be heated to 300 °C for 5 141 min. VOCs were transferred employing a transfer line heated at 200 °C to one column 142 (RESTEK-Rtx-5MS, PA, USA. w/integra-guard Crossbond 5 % diphenyl-95 % 143 dimethylpolysiloxane. 30 m, 0,25 mmID, 0,25 µm df) installed in a GC/MS (Thermo Fisher Scientific, model Trace 1300/ISQELTL, MA, USA). The working conditions of the GC for 144 the oven were in Split mode with a working temperature between 40 °C and 220 °C. Flow: 145 1,2 mL/min; Split Ratio: 10 °C/min, the transfer line temperature of the MS detector was 200 146 147 °C while the temperature ion-source was set at 250 °C. The qualitative identification of VOCs was carried out using the Chromeleon 7.2 software package (2013), which is compatible with 148 149 the NIST library (NIST Chemistry Webbook. 2010), using retention times observed in the 150 chromatograms. The experimental conditions are summarized in Table 2.

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Gas Chromatography/Mass	Temperature range	40 °C – 120 °C
Spectrometry	Flow	1,2 mL/min
	Split Ratio	10 °C/min
	Transfer line temperature	200 °C
	Ion source temperature	250 °C
	Column	30 m, 0,25 mmID, 0,25 μm df
Thermal Desorption	Driven media	Helium
	Time	1 min
	Hot trap temperature	300 °C
	Cooling system	20 °C
	Second heater	300 °C

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160 **3. RESULTS AND DISCUSSION**

161 Combustion processes are associated with a series effect on the environment, which is a 162 product of the produced compounds. Olsen *et al.* (2020) describe that, in a wood combustion 163 process, the particles and gases emitted can be divided into three classes: a) black carbon or 164 elemental carbon, which is associated with soot, i.e., carbon from incomplete combustion 165 processes that have a graphitic structure; b) organic carbon, associated with VOCs; and c) 166 inorganic species, i.e., ash particles.

Given the above, it should be established that for the urban areas of central-southern and southern Chile, around 90% of the population indicates that they consume firewood as the main source of heating in their homes, where approximately 38% is native firewood, 35% is eucalyptus firewood and 26% is a variety of species. It is worth mentioning that in large cities, the use of firewood for heating reaches 79%, while in smaller towns it reaches 98%. In addition, it can be seen that the highest concentration of households that consume firewood belong to a medium-low socioeconomic level (Bustos and Ferrada 2017; Reyes *et al.* 2020b).

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176 **3.1. VOCs by TD-GC/MS**

177 More than 150 compounds were identified in the samples analyzed, considering the moisture 178 conditions to which the wood was exposed (9 %, 25 %, and 33 %). However, many of these 179 compounds only appeared in one or two combustion stages (ignition, stable reload, and 180 quenching). Furthermore, the reliability of some identified compounds was less than 98 %, consistent with the NIST library (NIST Chemistry Webbook. 2010). Therefore, the inventory 181 182 of all compounds found throughout the experimental process was reduced to the compounds 183 shown in Table 3. In Table 3, VOCs were classified by families, name, odor threshold, and 184 their toxicity degree in humans. The compounds that were found in all the samples (18) were considered representative in terms of emissions, and these compounds constitutes around the 185 25 % of the total number of compounds of the samples (Hernández et al. 2019). Among the 186 VOCs identified, benzene and related compounds represented the most abundant group (45 187 % – 69 %), followed by oxygenates (21 % – 39 %), and aliphatic hydrocarbons (4 % – 23 188 %), depending on the stage of the combustion (ignition of Cycle 1, stable reload of Cycle 3, 189 190 and quenching of Cycle 3). The above results are similar to those reported by Evtyugina et 191 al. (2014) for emissions of the three types of wood (European beech, Pyrenean oak, and Black poplar). These woods are most used in residential combustion in southern Europe in slow-192 193 combustion stoves (wood stoves), reporting that the emissions of aromatic VOCs represented between (43 % - 60 %), oxygenates (26 % - 36 %), and aliphatic hydrocarbons (9 % - 16 %)194 195 %). Evtyugina et al. (2014) also analyzed the combustion of these three species of wood in 196 fireplaces, where benzene and the compounds related to this aromatic hydrocarbon continue 197 to represent the most abundant group (43 % - 45 %), followed by oxygenated VOCs (31 %198 -36%) and aliphatic hydrocarbons (16 \% - 18 %). Terpene compounds (4,5 % - 4,7 %) and

199 halogenated VOCs (0, 2% - 0, 5%) are also highlighted as relevant VOCs. On the other hand,

200 McDonald et al. (2000) analyzed the combustion of different types of soft and hardwood:

201 Ponderosa pine, Pinion pine, Missouri oak, Scrub oak, mixed hardwood (cottonwood, birch,

- 202 aspen), and synthetic logs. The results show that the most common VOCs in residential wood
- 203 combustion are ethane, acetylene, ethene, benzene, toluene, formaldehyde, and acetaldehyde.
- 204 Many of these compounds match with those reported in Table 3.

205	Table 2: VOCs in the combustion stage in a stove of Eucalyptus globulus.											
Families	Names	Formula	Odor	Humidity								
			threshold		9 %		25 %			33 %		
			ppm	Ign.	Ref.	Que.	Ign.	Ref.	Que.	Ign.	Ref.	Que.
				Cyc	Cycl	Cycle	Cycl	Cyc	Cycl	Cyc	Cyc	Cycle
				le 1	e 3	3	e 1	le 3	e 3	le 1	le 3	3
Aldehydes	Furfural	$C_5H_4O_2$	0,01000	X	X		X	X		Х	X	Х
	Benzaldehyde	C ₇ H ₆ O	0,00150	X	X		X	X	Х		X	X
	2-	$C_6H_6O_2$	-	-			Х	Х	-	Х	Х	Х
	Furancarboxaldehyde			(
	, 5-methyl					~						
Carboxylic	Acetic acid	CH ₃ COOH	1,00000	X	X	-	Х	X	X	Х	Х	Х
A.					Y							
Esters	propanoic acid 2-oxo-	$C_4H_6O_3$	0,02100	X	-	-	-	-	-	-	Х	-
D' '1	methyl ester	60	0.00000	Y			37		37			37
Dioxide	Carbon dioxide		0,00000		-	-	X	-	X	-	-	X
Aromatic H.	Benzene	C ₆ H ₆	4,68000	X	X	-	X	-	-	-	-	-
	Toluene	C ₆ H ₅ CH ₃	4,68000	X	X	-	X	-	-	-	X	X
	Ethylbenzene	C_8H_{10}	0,30000	X	X	-	X	-	-	-	-	-
	p-Xylene	$C_6H_4(CH_3)_2$	0,47000	X	X	-	X	X	X	X	X	-
	Benzofuran	C ₈ H ₆ O		X	-	-	-		-	X	X	X
	Benzene, 1-propynyl-	C ₉ H ₈		X	-	-	-		-			
	Naphthalene	С ₁₀ Н ₈	0,00190	X	X	-	X	X	-	X	X	X
	Styrene	C ₈ H ₈	0,10000	X	X	-	X	-	-	-	X	X
Cyclical H.	Biphenyl	$C_{12}H_{10}$	0,00052	X	X	-	X	-	-	-	-	X
	Phenylethyne	C ₈ H ₆	0,04700			-	X	-	-	-	-	-
	Acenaphthylene	C ₁₂ H ₈	-	X	X	-	-	-	-	X	-	-
	Furan, 2,5-dimethyl-	C_6H_8O	-	X	-	-	Х	-	-	-	X	X
	1,3-Cyclohexadiene	C ₆ H ₈	-	-	-	-	-	-	-	-	-	-
	Cyclotrisiloxane,	$C_6H_{18}O_5Si_4$	-	-	-	-	-	-	Х	-	-	Х
	hexamethyl											
	2-Methyl-2-phenyl-5	$C_{16}H_{15}N_3O_2$	-	-	X	-	-	-	-	-	-	-
	Butyrolactone	$C_4H_6O_2$	-	-		-	-	-	-	Х	-	Х
Alcohols	Phenol, 2-methoxy-	$C_7H_8O_2$	21,00000	Х	X	-	X	Х	X	Х	Х	X
	Creosol	$C_8H_{10}O_2$	90,0000	-	-	-	X	Х	-	Х	X	X
	Phenol, 3-methyl-	C_7H_8O	0,00005	-	-	-	Х	Х	-	-	Х	-

207 Furthermore, if we analyze in detail the VOCs measured in Table 3 for the Eucalyptus 208 globulus samples in the ignition, stable reload and quenching stages of the combustion 209 process, we observe that the reported molecules predominated and remained present 210 throughout the entire process of combustion while the experimental phase was carried out. 211 Languille et al. (2020) showed that in a period of three and a half months of winter in the Paris region, approximately sixteen VOCs are presented in the environment by wood 212 combustion, such as formaldehyde, methanol, acetonitrile, propene, acetaldehyde, acetic 213 acid, furan, butenal, methylacetate, methylfuran, methylbutenone, butandione, furfural, 214 215 furandione, benzenediol, and chlorobenzene. Also, Gaeggeler et al. (2008) found 216 approximately 51 VOCs with similar characteristics to those found by Languille et al. (2020), in a village of the Mesolcina valley in southern Switzerland, where most of the houses are 217 218 heated with wood.

Figure 2 shows the number of VOCs generated in the different combustion stages, where it 219 220 can be observed that the largest amount is present in the ignition stage, as well as in the final 221 stage. It can also be observed that there is a direct trend that as well as the moisture of wood 222 increases, the number of VOCs present in the samples increases from 29 compounds in dry wood (9 %) to 39 compounds in extra-humid wood (33 %). The above coincides with that 223 224 reported by Olsen et al. (2020), who describes that higher moisture content in wood promotes 225 higher PM and VOCs emissions due to the increase in organic content, where VOCs represent 226 41 % - 54 % of moisture content.

Ozil *et al.* (2009) showed that in the process of wood combustion in a stove, large amounts of CO and VOCs are generated during ignition after wood reload. A few minutes later, the wood ignites, and the gaseous emission of pollutants decrease, but the remaining coal significantly produces CO and VOCs emissions during the final stage. Therefore, CO and
VOCs are emitted mainly during the ignition and final combustion stages of a wood reload



under standard conditions.

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Figure 2: Number of VOCs by combustion stages.

Table 4 shows the trend in the ratio of benzene, toluene, and xylene at different moistures 236 237 and in the different combustion stages of Eucalyptus globulus wood. It can be observed that 238 in the ignition and stable reload stages, there is the presence of benzene (16 % and 32 %) and toluene (9 % and 8 %) for 9 % wood moistures, while in the final quenching stage, benzene 239 and toluene disappear for all samples (9 %, 25 % and 33 %). Special attention is paid to 240 xylene, which as the wood moisture increases (9 %, 25 % and 33 %), its composition 241 242 increases in the ignition and stable reload stages. In contrast, in the quenching stage, it 243 practically disappears. A study carried out by Guerrero et al. (2019) shows that the 244 combustion emissions of Eucalyptus globulus Labill increase PM 2,5 and polycyclic aromatic hydrocarbon by 11,4 % and 1,46 %, respectively, when they are at 25 % moisture 245 246 compared to the same wood at 0 % moisture.

Combustion cycle	Igniti	ion Cyc	le 1	Stable	reload (Cycle 3	Quenching Cycle 3			
Moisture content	9 %	25 %	33 %	9 %	25 %	33 %	9 %	25 %	33 %	
Benzene (%)	16,0	17,0		32,0						
p-xylene (%)	1,0	1,0	1,5	1,0	1,2	1,5		1,8		
Toluene (%)	9,0	6,0		8,0		3,0		-	3,5	

Table 4: Amount of benzene, toluene, and xylene in the combustion stage.

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The above shows that the wood combustion from different origins produces the emanation of VOCs into the environment, which implies that many of these molecules can cause effects on human health. Wöhler *et al.* (2016) showed that molecules such as benzo[a]pyrene and other polycyclic aromatic hydrocarbons such as benzene, formaldehyde, 1,3-butadiene, phenols, and cresols, produce damage when people are exposed to them.

256 Furthermore, from the molecules reported in this study, it has been shown that their presence 257 in the environment directly produces health damage, being benzene, toluene, and xylene of 258 particular important. Some authors report that the exposure of children to biomass 259 combustion has a direct incidence of chronic bronchitis (Smith et al. 2000) and induces acute 260 respiratory infections (Ezzati et al. 2002). Sinha et al. (2006) showed that the burning of 261 biomass fuel induces the level of benzene and toluene in the indoor air. Rinsky et al. (1987) 262 and IARC (1982) determined that exposure to benzene in the environment, even at low doses, 263 causes adverse health effects, particularly leukemia, aplastic anemia, bone marrow disorders, 264 and other types of cancer in humans. Given the above, it is known about the damage caused 265 to people by these molecules of anthropogenic origin reported and others. However, they are 266 still being generated into the environment either by the types of fuels used, the poor 267 combustion of the equipment used or the misuse of fuels. There is still no awareness that 268 wood is a natural fuel that must be at low moisture since this allows fewer VOCs to be emitted

269 into the environment, as demonstrated in this study.

270 **3.2. PM and combustion gas analysis**

Table 5 shows the behavior of the PM, moisture, and other combustion gases (CO, CO₂, NO_x)

272 emitted in the different stages of wood combustion. It can be observed that as the moisture

273 of the wood increase also increase the PM emissions.

274 275 Table 5: Analysis of particulate matter and common gases.

213	1							/				
Name	Unit		Dry wood	ł		Wet wood			Extra wet wood			
		9	9 % moistu	ire	25	5 % moist	ure	3.	ire			
Burning		Ignition	Reload	Quenchin	Ignition	Reload	Quenchin	Ignition	Reload	Quenchin		
stage		Cycle 1	Cycle 3	g Cycle 3	Cycle 1	Cycle 3	g Cycle 3	Cycle 1	Cycle 3	g Cycle 3		
O ₂	%	15,8	11,3	15,7	15,2	13,8	16,9	19,6	19,1	19,2		
PM (ref 13	mg/m ³	230,0	222,0	101,0	479,0	512,0	156,0	4953,0	9031,0	3639,0		
%O ₂)	-											
CO	mg/m ³	2892,0	1585,0	5022,0	4922,0	6318,0	8193,0	22914,0	29278,0	25054,0		
CO ₂ (ref.13	%vol	2,2	4,1	2,2	2,5	3,0	1,6	0,6	0,9	0,8		
%O ₂)				A		p.						
NO _x (ref.13	ppm	11,7	20,6	10,7	10,7	15,7	7,2	12,5	19,9	16,4		
%O ₂)												
Gas	°C	115,4	275,1	224,6	139,6	242,1	222,0	53,4	88,5	82,6		
temperature				O								
Ambient	°C	18,6	25,9	28,7	18,9	26,5	29,3	22,2	26,3	26,3		
temperature												
Air ratio (λ)		4,6	2,2	3,9	4,2	3,0	5,2	14,1	9,1	10,2		
Efficiency	%	88,1	84,2	76,0	86,0	78,9	67,6	78,2	73,0	73,6		
(η)				<i></i>								

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As mentioned above, Table 5 shows an increase in pollutants in terms of the moisture present in the wood with a varied behavior in the different combustion stages for the monitored parameters. Thus, O_2 and PM present the highest concentration values in the stages of ignition and stable reload with a peak of 19,6 % and 9031 mg/m³, respectively. For CO, the stable reloads, and quenching stages present a higher index with a maximum value of 29,3 mg/m³ with 35 % moisture. Further, CO₂ and NO_x compounds maintained a higher concentration in the stable reload stage of wood, where the highest value of CO₂ and NO_x were found in the lower moisture wood, which were 4,1 % vol and 20,6 ppm, respectively. The above values are comparable to those reported by Gonçalves *et al.* (2010), who characterize PM10 emissions from various types of wood commonly used in Portugal in wood stoves. Emission factors ranged between 1,12 g/kg \pm 0,25 g/kg and 2,89 g/kg \pm 0,90 g/kg of wood burned (dry basis). *Pine* and *Acacia longifolia* generate the lowest particle emissions, while the highest levels were produced by oak wood and *Eucalyptus globulus*.

The temperature reached by dry wood (9 % moisture) is the highest recorded in the study and, in the same way, is that reach a higher percentage of efficiency with 88,1 % because they give off a higher calorific value and a temperature of 275,1°C for gases in the stable reload stage of combustion. The atmospheric pollutants produced by fuel batches with higher moisture concentrations have a significant impact on health, particularly in people with a risk of respiratory diseases, according to studies by Kim *et al.* (2011) and Poláčik *et al.* (2021).

On the one hand, living in an area with high PM levels produces pulmonary retention of large numbers of particles, some of which appear to be the result of combustion. The above was detected when comparing the lungs of residents in Mexico City with residents in Vancouver, Canada, whose PM mean (<10 μ m aerodynamic diameter) were 66 μ g/m³ and 14 μ g/m³, respectively (Smith *et al.* 2000). It has been reported that 96 % of the particles detected in autopsy lung tissue have a diameter <2,5 μ m, evidencing the importance of PM 2,5 as an atmospheric pollutant (Matus and Oyarzún 2019).

303 Oyarzún (2010) states that when considering the environmental conditions and the 304 dissolution of compounds under high moisture and low temperatures, greater exposure to 305 these compounds can be observed in the risk sectors, producing more significant complications in winter times. Nascimento *et al.* (2020) indicate a greater relative risk of 1,14
(95 % CI: 1,09 – 1,20) on the day of exposure, presenting acute respiratory diseases per day
of exposure to high concentrations of PM 10. Canha *et al.* (2011) report evidence of increased
respiratory diseases, such as rhinitis, in children during the winter season, associated with
increased total PM.

311 According to Olsen et al. (2020), health impacts make the quality of new wood stoves 312 relevant. Several countries are controlling this by compulsory certification in compliance 313 with stipulated national standards. Thus, US-EPA and the Canadian standard certify wood stoves according to a weighted maximum average emission rate of 4,5 g/h PM. PM limits for 314 Australia and New Zealand are 2,5 g/kg and 1,5 g/kg, respectively. Most EU member states 315 currently do not regulate wood stove emissions (except, e.g., Denmark, Norway, Sweden, 316 Austria, and Germany). However, the newly adopted European Union Directive on Eco-317 design for wood stoves, coming into force in 2022, will require compliance with maximum 318 PM emissions of 5 g per kg of fuel (dry matter). 319

Although combustion gases, such as VOCs and PM, are released into the environment due to wood combustion, it is important to mention that its moisture is a critical factor in the analysis of results since it considerably increases the presence of these pollutants in the close environment.

Finally, the number of compounds in the emissions produced by the combustion of *Eucalyptus globulus* is directly related to the moisture in the wood. In terms of toxicity and risks to human health, the environmental conditions of moisture and temperature are relevant factors since they could make it difficult to dissolve compounds harmful to human health.

329 **3.3.** Diffusion on compounds in the environment

VOCs usually have a high vapor pressure at room temperature; hence, these compounds are produced from many sources, including industrial, combustion, and conveyance sources (Lancaster 2002). Also, diffusion and evaporation are the most important mechanism that drives VOCs emission to the atmosphere. Both mechanisms are sensitive to the changes in atmospheric conditions and the source of the emission (Wolkoff 1998)

335 Therefore, once the VOCs and PM are in the environment, their dispersion, transformation, 336 and solubility will depend mainly on the meteorological conditions. Further, the emissions 337 depend on the relative humidity and temperature, which is shown in Figure 3. The 338 temperature inversions in certain geographical places and periods of low temperatures are a phenomenon that directly affects the dispersion of VOCs and PM in the environment, 339 implying that if more stoves are burned in one determined place, the concentrations of these 340 341 pullulans will increase. Rokoff et al. (2017) show that the combustion of wet wood generates 342 incomplete combustion and higher emissions, affecting the valleys prone to wintertime temperature inversions, in which cool, polluted air is trapped near the ground under warmer 343 344 air. Burschnel et al. (2003) describe that PM concentrations produced between April and September in Chile are the rainfall product and the temperature inversion. The dispersion of 345 pollutants is difficult in the urban sector. 346

Additionally, Figure 3 shows that the average temperatures are low (10 °C), and the average relative humidity is high (70 %) for the winter and autumn in Chile. This situation is directly related to the increase in VOCs and PM in the environment, placing these molecules at a lower height and leaving them in contact with people (Csavina *et al.* 2014). Radaideh (2017) describes that as temperatures drop and relative humidity increases, concentrations of VOCs and CO, SO₂, and O₃ also increase. Consequently, there is a direct relationship between
 environmental phenomena and the incidence of pollution.

354 Finally, if we analyze in detail the toluene, benzene, and xylene molecules described in 355 Tables 2 and 3, which are part of the VOCs listing, these molecules have a low polarity. The 356 latter means that when there is a high amount of relative humidity (polar H₂O) in the 357 environment, their dispersion and solubility decrease, implying that they remain in the 358 environment for longer. Moreover, if we consider the Henry constant based on these 359 phenomena, we can say that the higher the Henry constant for considered VOCs, the less 360 solubility exists for these molecules in an environment where the relative moisture is high 361 (Zhou et al. 2017).



366 4. CONCLUSIONS

This work has been devoted to characterizing the concentration levels of VOCs and PM in the combustion of *Eucalyptus globulus* wood. The humidity levels have been considered as a critical variable on the emissions. For the above, wood samples with different moisture

levels were used. Both VOCs and PM amounts increase as well as the humidity of biomassincrease.

On the one hand, other volatile compounds, particularly aromatic species as toluene, benzene, and xylene, were found in the exhaust gases. Aromatics compounds were only found in the ignition and stable reload stage, being their concentration in later stages practically nonexistent. On the other hand, CO_2 and NO_x have predominance in the reload stage. The solubility and dispersion of VOCs molecules have been compared with weather conditions, particularly temperature and relative humidity of the air, founding a direct correlation

between these atmospheric variables and the impact of the emissions.

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