

VOCs AND PM LISTING OF *Eucalyptus globulus* COMBUSTION IN RESIDENTIAL WOOD STOVES

*Francisco Henríquez*¹

<https://orcid.org/0000-0001-7234-3369>

Diógenes Hernández^{1,2,4,*}

<https://orcid.org/0000-0002-3857-7492>

*Felipe Varas-Concha*³

<https://orcid.org/0000-0002-7566-8326>

*Camila Gutierrez*¹

<https://orcid.org/0000-0002-1194-1338>

*Héctor Quinteros-Lama*¹

<https://orcid.org/0000-0001-8953-6140>

Jorge O. Morales-Ferreiro^{1,4}

<https://orcid.org/0000-0003-1106-2832>

ABSTRACT

Pollutant residential emissions from wood stoves have significant impacts both on the environment and people's health. The above makes it essential to know the types of volatile organic compounds emitted during combustion and explore their relationship with particulate matter and greenhouse gas emissions. This paper studies and analyzes these emissions using *Eucalyptus globulus* as fuel varying its moisture levels. Emissions were determined using an adapted commercial stove. The concentration levels of volatile organic compounds and particulate matter increase with the moisture of wood. When analyzing volatile organic compounds, particulate matter, and O₂ with the combustion stages of wood, it is found that their concentrations were higher in the ignition and the reload stage. The concentrations of CO₂ and NO_x were higher in the reload stage. Other chemical compounds, such as toluene, xylene, and benzene, were also found within the volatile organic compounds listing, which increased their concentration in the ignition and stable reload stages. However, in the 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 molecules remain in the environment in direct contact with the people living in those places.

Keywords: Biomass combustion, boiler load, particulate matter, volatile organic compounds, volatile organic compounds emission, wood stove.

¹Universidad de Talca. Facultad de Ingeniería. Departamento de Tecnologías Industriales. Curicó, Chile.

²Universidad de Talca. Instituto de Química de Recursos Naturales. Curicó, Chile.

³Universidad de Talca. Facultad de Ingeniería. Centro Tecnológico Kipus. Curicó, Chile.

⁴Universidad de Talca. Facultad de Ingeniería. Centro Conversión de Energías. Curicó, Chile.

*Corresponding author: dhernandez@utalca.cl

Accepted: 04.12.2022 Received: 11.05.2021

INTRODUCTION

In the history of humankind, residential heating has been a basic need to maintain adequate thermal comfort inside the homes. Different systems have been developed for this need, but 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 % of the world's population (Sáenz-Ceja *et al.* 2017, FAO 2017). Besides, 80 % of wood comes from forest wood products (Berrueta *et al.* 2017). The wood comes from different species: in urban areas, 95 % of wood corresponds to exotic species (50 % *Eucalyptus globulus*, 37 % fruit trees, and 8 % others), 4 % to waste wood and only 1 % 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 wood (Reyes *et al.* 2020a).

Chile is one of the pioneers in this use of *Eucalyptus globulus* for combustion, with an available planted area of 860317 hectares (Molina-Mercader *et al.* 2019). In the process of wood combustion in stoves, a variety of pollutants are produced such as volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), particulate matter (PM), carbon monoxide (CO), carbon dioxide (CO₂) and NO_x (Vicente *et al.* 2020, Guerrero *et al.* 2019, Weinstein *et al.* 2020, Naeher *et al.* 2007, Bruce *et al.* 2000). These gases are released into the environment and remain dispersed based on existing climatic conditions. In areas with valley topography, temperature inversions at night limit the dispersion of pollutants from sources of terrestrial origin (Allen *et al.* 2011). At night, atmospheric stability varies 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 generates that these VOCs. Other gases and PM are located at a lower altitude, producing direct contact with the communities living in those places.

Different studies have referenced the effects on people's health due to wood combustion, where acute upper respiratory tract infection, reduced lung function, and cough, among others, are the most frequently reported (Aliyu *et al.* 2015, Basagaña *et al.* 2015, Satsangi *et al.* 2014). Additionally, Naeher (2007) describes that there are about 200 types of VOCs in wood combustion known as Hazardous Air Pollutants, where many of these are of particular interest due to their carcinogenic effect (Grineski *et al.* 2016, Wu *et al.* 2009). Within this group are benzo[a]pyrene, benzene, toluene, xylene, and ethylbenzene, which even in very low concentrations produce severe effects on people (International Agency for Research on 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 *Eucalyptus globulus*, considering different percentages of moisture and combustion stages (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 drying process before combustion. Price-Allison *et al.* (2019) reports that the higher the percentage of relative humidity in wood, the more gases are produced in wood combustion, indicating that moisture can be a key factor in these phenomena. The above affecting the listing of VOCs and PM emissions of wood, differing from those already reported for other types of wood since the type of wood is one of the factors that most affect emissions (McDonald *et al.* 2000).

MATERIALS AND METHODS

Experimental design

The tests were carried out in the laboratory of emissions of Kipus Technology Center at Universidad de Talca, using a single-room wood stove from the Chilean manufacturer Amesti, model Scantek 360. The stove has a nominal heat output of 8,5 kW and, according to the manufacturer, an efficiency of 70 %. The stove operates with a natural draft, and it has a staged air supply with primary and secondary air entries. The secondary air source can be controlled manually via air damper. The stove tests were carried out 3 samples of with 30 cm length of *Eucalyptus globulus* wood, the typical wood used in Chile for residential heating. Three experiments were run using different relative humidity of wood: 1 sample dry wood (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 in different combustion stages (ignition, reload and quenching phases). Gaseous exhaust gas components were measured continuously (CO_2 , CO , O_2 , NO , NO_2). PM was measured with single batch samples and VOCs were sampled in batch measurements by duplicate samples. 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 wet wood logs; 2,4 kg of extra-wet wood logs), using the method reported by the Chilean Superintendence of Energy and Fuels (SEC 2020).

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

Table 1: Measurement technology.

Device	Principle	Components	Range	Accuracy
Wöhler SM 500	Gravimetric	PM	0 - 1000 mg/m^3	$\pm 0,3 \text{ mg}$
	Electrochemical sensor	O_2	0 - 21 vol%	$\pm 0,3 \text{ vol}\%$
	Electrochemical sensor	CO	0 - 100000 ppm	$\pm 100 \text{ ppm}$
Testo 350 XL	Electrochemical sensor	NO	0 - 99 ppm	$\pm 5 \text{ ppm}$
	Electrochemical sensor	NO_2	0 - 99,9 ppm	$\pm 5 \text{ ppm}$
	Infrared sensor	CO_2	0 - 50 vol%	$\pm 0,3 \text{ vol}\%$
Minipo MWD-14A	Electrical resistance	Relative humidity	5,0 - 40 %	$\pm 1 \%$

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

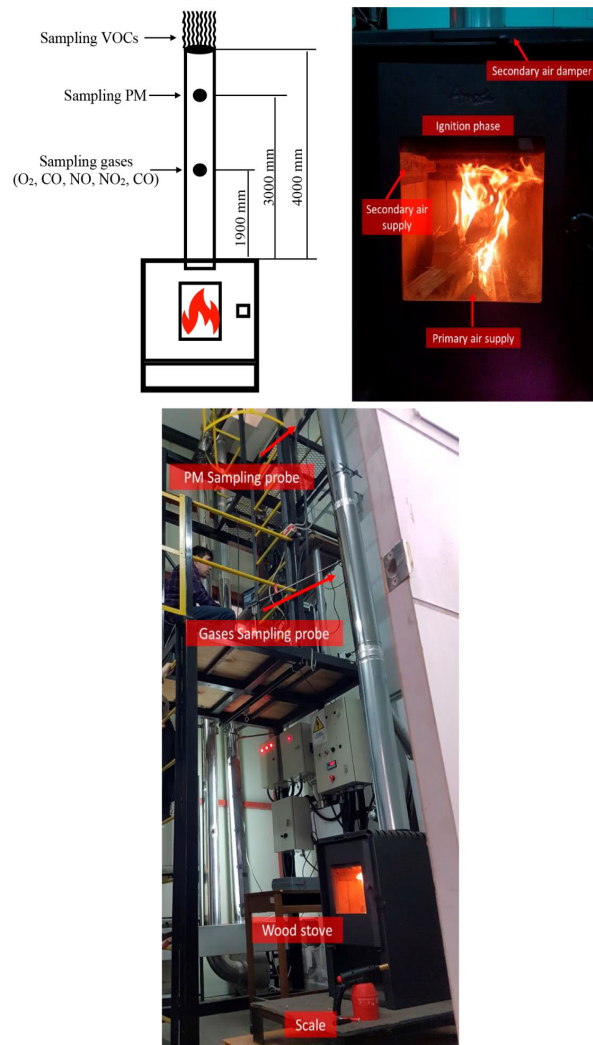


Figure 1: Scheme for taking samples and images of the system used during the experiments.

Conditions of thermal desorption-gas chromatography/mass spectrometry (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 programmed at 300 °C and then cooled to 20 °C in the cold trap to be heated to 300 °C for 5 min. VOCs were transferred employing a transfer line heated at 200 °C to one column (RESTEK-Rtx-5MS, PA, USA. w/integra-guard Crossbond 5 % diphenyl-95 % dimethylpolysiloxane. 30 m; 0,25 mmID;3 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 the oven were in Split mode with a working temperature between 40 °C and 220 °C. Flow: 1,2 mL/min; Split Ratio: 10 °C/min, the transfer line temperature of the MS detector was 200 °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 the NIST library (NIST Chemistry Webbook 2010), using retention times observed in the chromatograms. The experimental conditions are summarized in Table 2.

Table 2: Working conditions for the TD-GC/MS.

Gas Chromatography/Mass Spectrometry	Temperature range	40 °C - 120 °C
	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

RESULTS AND DISCUSSION

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

VOCs by TD-GC/MS

More than 150 compounds were identified in the samples analyzed, considering the moisture conditions to which the wood was exposed (9 %, 25 %, and 33 %). However, many of these compounds only appeared in one or two combustion stages (ignition, stable reload, and quenching). Furthermore, the reliability of some identified compounds was less than 98 %, consistent with the NIST library (NIST Chemistry Webbook. 2010). Therefore, the inventory of all compounds found throughout the experimental process was reduced to the compounds shown in Table 3. In Table 3, VOCs were classified by families, name, odor threshold, and 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 25 % of the total number of compounds of the samples (Hernández *et al.* 2019). Among the VOCs identified, benzene and related compounds represented the most abundant group (45 % - 69 %), followed by oxygenates (21 % - 39 %), and aliphatic hydrocarbons (4 % - 23 %), depending on the stage of the combustion (ignition of Cycle 1, stable reload of Cycle 3, and quenching of Cycle 3). The above results are similar to those reported by Evtuyugina *et 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-combustion stoves (wood stoves), reporting that the emissions of aromatic VOCs represented between (43 % - 60 %), oxygenates (26 % - 36 %), and aliphatic hydrocarbons (9 % - 16 %). Evtuyugina *et al.* (2014) also analyzed the combustion of these three species of wood in fireplaces, where benzene and the compounds related to this aromatic hydrocarbon continue to represent the most abundant group (43 % - 45 %), followed by oxygenated VOCs (31 % - 36 %) and aliphatic hydrocarbons (16 % - 18 %). Terpene compounds (4,5 % - 4,7 %) and halogenated VOCs (0,2 % - 0,5 %) are also highlighted as relevant VOCs. On the other hand, McDonald *et al.* (2000) analyzed the combustion of different types of soft and hardwood: *Ponderosa pine*, *Pinion pine*, *Missouri oak*, *Scrub oak*, mixed hardwood (cottonwood, birch, aspen), and synthetic logs. The results show that the most common VOCs in residential wood

combustion are ethane, acetylene, ethene, benzene, toluene, formaldehyde, and acetaldehyde. Many of these compounds match with those reported in Table 3.

Table 3: VOCs in the combustion stage in a stove of *Eucalyptus globulus*.

Families	Names	Formula	Odor threshold ppm	Humidity								
				9 %			25 %			33 %		
				Ign. Cycle 1	Ref. Cycle 3	Que. Cycle 3	Ign. Cycle 1	Ref. Cycle 3	Que. Cycle 3	Ign. Cycle 1	Ref. Cycle 3	Que. Cycle 3
Aldehydes	Furfural	C ₅ H ₄ O ₂	0,01000	X	X		X	X		X	X	X
	Benzaldehyde	C ₇ H ₆ O	0,00150	X	X		X	X	X		X	X
	2-Furancarboxaldehyde 5-methyl	C ₆ H ₆ O ₂	-	-	-	-	X	X	-	X	X	X
Carboxylic A.	Acetic acid	CH ₃ COOH	1	X	X	-	X	X	X	X	X	X
Esters	propanoic acid 2-oxo-methyl ester	C ₄ H ₆ O ₃	0,02100	X	-	-	-	-	-	-	X	-
Dioxide	Carbon dioxide	CO ₂	0	--	-	-	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 ₈ H ₁₀	0,30000	X	X	-	X	-	-	-	-	-
	p-Xylene	C ₆ H 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	C ₁₀ H ₈	0,00190	X	X	-	X	X	-	X	X	X
Cyclical H.	Styrene	C ₈ H ₈	0,10000	X	X	-	X	-	-	-	X	X
	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-1,3-Cyclohexadiene	C ₆ H ₈ O	-	X	-	-	X	-	-	-	X	X
	Cyclotrisiloxane, hexamethyl	C ₆ H ₁₈ O ₅ Si ₄	-	-	-	-	-	-	X	-	-	X
	2-Methyl-2-phenyl-5-Butyrolactone	C ₁₆ H ₁₅ N ₃ O ₂	-	-	X	-	-	-	-	-	-	-
Alcohols	Phenol, 2-methoxy-	C ₇ H ₈ O ₂	21	X	X	-	X	X	X	X	X	X
	Creosol	C ₈ H ₁₀ O ₂	90	-	-	-	X	X	-	X	X	X
	Phenol, 3-methyl-	C ₇ H ₈ O	0,00005	-	-	-	X	X	-	-	X	-

Furthermore, if we analyze in detail the VOCs measured in Table 3 for the *Eucalyptus globulus* samples in the ignition, stable reload and quenching stages of the combustion process, we observe that the reported molecules predominated and remained present throughout the entire process of combustion while the experimental phase was carried out. 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 combustion, such as formaldehyde, methanol, acetonitrile, propene, acetaldehyde, acetic acid, furan, butenal, methylacetate, methylfuran, methylbutenone, butandione, furfural, furandione, benzenediol, and chlorobenzene. Also, Gaeggeler *et al.* (2008) found 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 heated with wood.

Figure 2 shows the number of VOCs generated in the different combustion stages, where it can be observed that the largest amount is present in the ignition stage, as well as in the final stage. It can also be observed that there is a direct trend that as well as the moisture of wood 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 reported by Olsen *et al.* (2020), who describes that higher moisture content in wood promotes higher PM and VOCs emissions due to the increase in organic content, where VOCs represent 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.

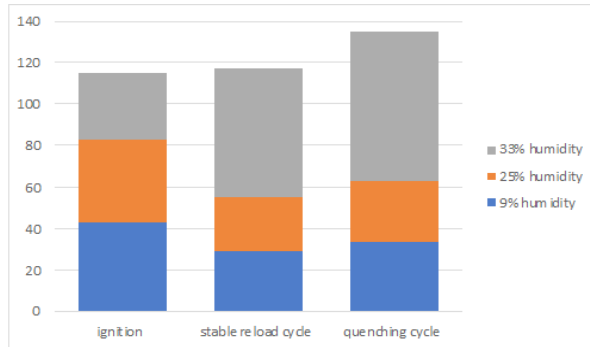


Figure 2: Number of VOCs by combustion stages.

Table 4 shows the trend in the ratio of benzene, toluene, and xylene at different moistures and in the different combustion stages of *Eucalyptus globulus* wood. It can be observed that 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 and toluene disappear for all samples (9 %, 25 % and 33 %). Special attention is paid to xylene, which as the wood moisture increases (9 %, 25 % and 33 %), its composition increases in the ignition and stable reload stages. In contrast, in the quenching stage, it practically disappears. A study carried out by Guerrero *et al.* (2019) shows that the 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 compared to the same wood at 0 % moisture.

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

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

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.

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

ronment, as demonstrated in this study.

PM and combustion gas analysis

Table 5 shows the behavior of the PM, moisture, and other combustion gases (CO , CO_2 , NO_x) emitted in the different stages of wood combustion. It can be observed that as the moisture of the wood increase also increase the PM emissions.

Table 5: Analysis of particulate matter and common gases.

Name	Unit	Dry wood 9 % moisture			Wet wood 25 % moisture			Extra wet wood 33 % moisture		
		Ignition Cycle 1	Reload Cycle 3	Quenchin g Cycle 3	Ignition Cycle 1	Reload Cycle 3	Quenchin g Cycle 3	Ignition Cycle 1	Reload Cycle 3	Quenchin 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 % O_2)	mg/m^3	230	222	101	479	512	156	4953	9031	3639
CO	mg/m^3	2892	1585	5022	4922	6318	8193	22914	29278	25054
CO_2 (ref.13 % O_2)	%vol	2,2	4,1	2,2	2,5	3	1,6	0,6	0,9	0,8
NO_x (ref.13 % O_2)	ppm	11,7	20,6	10,7	10,7	15,7	7,2	12,5	19,9	16,4
Gas temperature	$^\circ\text{C}$	115,4	275,1	224,6	139,6	242,1	222	53,4	88,5	82,6
Ambient temperature	$^\circ\text{C}$	18,6	25,9	28,7	18,9	26,5	29,3	22,2	26,3	26,3
Air ratio (λ)		4,6	2,2	3,9	4,2	3	5,2	14,1	9,1	10,2
Efficiency (η)	%	88,1	84,2	76	86	78,9	67,6	78,2	73	73,6

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/m^3 , respectively. For CO, the stable reloads, and quenching stages present a higher index with a maximum value of 29,3 mg/m^3 with 35 % moisture. Further, CO_2 and NO_x compounds maintained a higher concentration in the stable reload stage of wood, where the highest value of CO_2 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 $\text{g}/\text{kg} \pm 0,25 \text{ g}/\text{kg}$ and 2,89 $\text{g}/\text{kg} \pm 0,90 \text{ g}/\text{kg}$ 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 $^\circ\text{C}$ 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 μm aerodynamic diameter) were 66 $\mu\text{g}/\text{m}^3$ and 14 $\mu\text{g}/\text{m}^3$, respectively (Smith *et al.* 2000). It has been reported that 96 % of the particles detected in autopsy lung tissue have a diameter <2,5 μm , evidencing the importance of PM 2,5 as an atmospheric pollutant (Matus and Oyarzún 2019).

Oyarzún (2010) states that when considering the environmental conditions and the dissolution of compounds under high moisture and low temperatures, greater exposure to 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.

According to Olsen *et al.* (2020), health impacts make the quality of new wood stoves relevant. Several countries are controlling this by compulsory certification in compliance 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 Australia and New Zealand are 2,5 g/kg and 1,5 g/kg, respectively. Most EU member states currently do not regulate wood stove emissions (except, e.g., Denmark, Norway, Sweden, Austria, and Germany). However, the newly adopted European Union Directive on Eco-design for wood stoves, coming into force in 2022, will require compliance with maximum PM emissions of 5 g per kg of fuel (dry matter).

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.

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)

Therefore, once the VOCs and PM are in the environment, their dispersion, transformation, and solubility will depend mainly on the meteorological conditions. Further, the emissions depend on the relative humidity and temperature, which is shown in Figure 3. The 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, implying that if more stoves are burned in one determined place, the concentrations of these pollutants will increase. Rokoff *et al.* (2017) show that the combustion of wet wood generates 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 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 pollutants is difficult in the urban sector.

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.

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

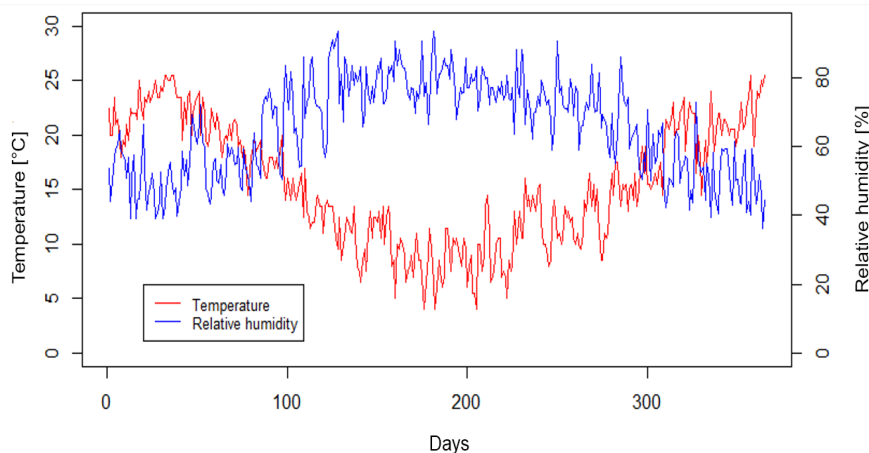


Figure 3: Average daily temperature and relative humidity in one year in Chile (1 - January to 31 - December).

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 biomass increase.

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 non-existent. On the other hand, CO₂ 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.

ACKNOWLEDGEMENTS

Diógenes Hernández, acknowledges funding from FONDECYT, Chile (Grant N°. 11200398). “Characterization of VOCs, a way to determine the degradation, storage and recovery of agroindustrial waste”

REFERENCES

Aliyu, A.S.; Ramli, A.T.; Saleh, M.A. 2015. Assessment of potential human health and environmental impacts of a nuclear power plant (NPP) based on atmospheric dispersion modeling. *Atmósfera* 28(1): 13-26. [https://doi.org/10.1016/S0187-6236\(15\)72156-9](https://doi.org/10.1016/S0187-6236(15)72156-9)

Allen, G.A.; Miller, P.J.; Rector, L.J.; Brauer, M.; Su, J.G. 2011. Characterization of valley winter woodsmoke concentrations in Northern NY using highly time-resolved measurements. *Aerosol and Air Quality Research* 11(5): 519-530. <https://doi.org/10.4209/aaqr.2011.03.0031>

Basagaña, X.; Jacquemin, B.; Karanasiou, A.; Ostro, B.; Querol, X.; Agis, D.; Alessandrini, E.; Alguacil, J.; Artiñano, B.; Catrambone, M.; de la Rosa, J.; Díaz, J.; Faustini, A.; Ferrari, S.; Forastiere, F.; Katsouyanni, K.; Linares, C.; Perrino, C.; Ranzi, A.; Ricciardelli, I.; Samoli, E.; Zauli-Sajani, S.; Sunyer, J.; Stafoggia, M. 2015. Short-term effects of particulate matter constituents on daily hospitalizations and mortality in five South-European cities: Results from the MED-PARTICLES project. *Environment International* 75: 151-158. <https://doi.org/10.1016/j.envint.2014.11.011>

Bede-Ojimadu, O.; Orisakwe, O.E. 2020. Exposure to Wood Smoke and Associated Health Effects in Sub-Saharan Africa: A Systematic Review. *Annals of Global Health* 86(1): e32. <http://doi.org/10.5334/aogh.2725>

Berrueta, V.M.; Serrano-Medrano, M.; García-Bustamante, C.; Astier, M.; Maserà, O. 2017. Promoting sustainable local development of rural communities and mitigating climate change: the case of Mexico's Patsari improved cookstove program. *Climatic Change* 140: 63-77. <https://doi.org/10.1007/s10584-015-1523-y>

Bustos, Y.; Ferrada, L.M. 2017. Consumo residencial de leña, análisis para la ciudad de Osorno en Chile. *Idesia* 35(2): 95-105. <https://doi.org/10.4067/S0718-34292017005000024>

Bruce, N.; Perez-Padilla, R.; Albalak, R. 2000. Indoor air pollution in developing countries: A major environmental and public health challenge. *Bulletin of the World Health Organization* 78(9): 1078-1092. <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC2560841/pdf/11019457.pdf>

Burschnel, H.; Hernández, A.; Lobos, M. 2003. *Leña: Una fuente energética renovable para Chile*. Editorial Universitaria: Santiago, Chile.

Canha, N.; Almeida, M.; do Carmo, M.; Almeida, S.; Wolterbeek, H. 2011. Seasonal variation of total particulate matter and children respiratory diseases at Lisbon primary schools using passive methods. *Procedia Environmental Sciences* 4: 170-183. <https://doi.org/10.1016/j.proenv.2011.03.021>

Csavina, J.; Field, J.; Félix, O.; Corral-Avitia, A.; Sáez, A.; Betterton, E. 2014. Effect of Wind Speed and Relative Humidity on Atmospheric Dust Concentrations in Semi-Arid Climates. *Science of The Total Environment* 487: 82-90. <https://doi.org/10.1016/j.scitotenv.2014.03.138>

CHROMELEON. 2013. Chromeleon 7.2 software package. <https://www.thermofisher.com/order/catalog/product/CHROMELEON7#/CHROMELEON7>

De Nevers, N. 1998. *Ingeniería de control de la contaminación del aire*. Mac Graw-Hill Interamericana: México.

Evtuygina, M.; Alves, C.; Calvo, A.; Nunes, T.; Tarelho, L.; Duarte, M.; Prozil, S.; Evtuguin, D.; Casimiro, Pio. 2014. VOC emissions from residential combustion of Southern and mid-European. *Atmospheric Environment* 89: 90-98. <https://doi.org/10.1016/j.atmosenv.2013.10.050>

Ezzati, M.; Salish, H.; Kammen, D. 2002. The contributions of emission and spatial microenvironments to exposure to indoor air pollutions from biomass combustion in Kenya. *Environmental Health Perspectives* 108(9): 833-839. <https://doi.org/10.1289/ehp.00108833>

FAO. 2017. Incentivizing Sustainable Wood Energy in Sub-Saharan Africa: A Way Forward for Policy. Food and Agriculture Organization of the United Nations: Rome, Italy. <http://www.fao.org/3/a0806t/a0806t00.htm>

Gaeggeler, K.; Prevot, A.; Dommen, J.; Legreid, G.; Reimann, S.; Baltensperger, U. 2008. Residential wood burning in an Alpine valley as a source for oxygenated volatile organic compounds, hydrocarbons and organic acids. *Atmospheric Environment* 42(35): 8278-8287. <https://doi.org/10.1016/j.atmosenv.2008.07.038>

Gonçalves, C.; Alves, C.; Evtuygina, M.; Mirante, F.; Pio, C.; Caseiro, A.; Schmidl, C.; Bauer, H.; Carvalho, F. 2010. Characterisation of PM10 emissions from woodstove combustion of common woods grown in Portugal. *Atmospheric Environment* 44: 4474-4480. <https://doi.org/10.1016/j.atmosenv.2010.07.026>

Grineski, S.; Clark-Reyna, S.; Collins, T. 2016. Collins, School-based exposure to hazardous air pollutants and grade point average: A multi-level study. *Environmental Research* 147: 164-171. <https://doi.org/10.1016/j.envres.2016.02.004>

Guerrero, F.; Yáñez, K.; Vidal, V.; Cereceda-Balic, F. 2019. Effects of wood moisture on emission factors for PM_{2.5}, particle numbers and particulate-phase PAHs from *Eucalyptus globulus* combustion using a controlled combustion chamber for emissions. *Science of The Total Environment* 648: 737-744. <https://doi.org/10.1016/j.scitotenv.2018.08.057>

Haro-Velasteguí, A.; Limáico-Nieto, C.; Perugachi-Cahueñas, N.; Fernández-Parra, M. 2018. Evaluación de la Estabilidad Atmosférica Bajo Condiciones Físicas y Meteorológicas del Altiplano Ecuatoriano. *Revista Brasileira de Meteorologia* 33(2): 336-343. <https://doi.org/10.1590/0102-7786332015>

Hernández, D.; Quinteros-Lamas, H.; Tenreiro, C.; Gabriel, D. 2019. Assessing Concentration Changes of Odorant Compounds in the Thermal-Mechanical Drying Phase of Sediment-Like Wastes from Olive Oil Extraction. *Applied Sciences* 9(3): 519. <https://doi.org/10.3390/app9030519>

IARC. 1982. Some industrial chemical and dyestuffs. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. IARC: Lyon, France. 29: 95-148. <https://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Some-Industrial-Chemicals-And-Dyestuffs-1982>

IARC. 2015. Monographs on the Evaluation of Carcinogenic Risks to Humans: Outdoor Air Pollution. In *IARC monographs* 109th edition. IARC: Lyon, France. 109: 35-50. <https://publications.iarc.fr/Book-And-Report-Series/Iarc-Monographs-On-The-Identification-Of-Carcinogenic-Hazards-To-Humans/Outdoor-Air-Pollution-2015>

Kim, K.; Jahan, S.; Kabir, E. 2011. A review of diseases associated with household air pollution due to the use of biomass fuels. *Journal of Hazardous Materials* 192(2): 425-431. <https://doi.org/10.1016/j.jhazmat.2011.05.087>

Languille, B.; Gros, V.; Petit, J.E.; Honoré, C.; Baudic, A.; Perrussel, O.; Forest, G.; Michound, V.; Truong, F.; Bonnaire, N.; Sarda-Estève, R., Delmotte, M.; Feron, A.; Maisonneuve, F.; Gaimoz, C.; Formenti, P.; Kotthaus, S.; Haefelin, M.; Favez, O. 2020. Wood burning: A major source of Volatile Organic Compounds during wintertime in the Paris region *Science of The Total Environment* 711: 135055. <https://doi.org/10.1016/j.scitotenv.2019.135055>

Lancaster, M. 2002. *Green chemistry: A introductory text*. Royal Society of Chemistry: UK. 163-168. <https://doi.org/10.1039/9781847551009>

Molina-Mercader, G.; Angulo, A.; Sanfuentes, E.; Hasbún, R.; Olivares, T.; Castillo-Salazar, M.; Goycoolea, C. 2019. Detección y distribución de *Ophelimus migdanorum* y su posible biocontrolador *Closterocerus chamaeleon* en áreas productivas de *Eucalyptus globulus* en Chile. *Chilean Journal of Agricultural Research* 79(3): 337-346. <https://dx.doi.org/10.4067/S0718-58392019000300337>

Matus, P.; Oyarzún, M. 2019. Impacto del Material Particulado aéreo (MP_{2,5}) sobre las hospitalizaciones por enfermedades respiratorias en niños: estudio caso-control alterno. *Revista Chilena de Pediatría* 90(2): 166-174. <http://dx.doi.org/10.32641/rchped.v90i2.750>

McDonald, J.; Zielinska, B.; Fujita, E.; Sagebiel, J.; Chow, J.; Watson, J. 2000. Fine particle and gaseous emission rates from residential wood combustion. *Environmental Science & Technology* 34(11): 2080-2091. <https://doi.org/10.1021/es9909632>

Naeher, L.; Brauer, M.; Lipsett, M.; Zelikoff, J.; Simpson, C.; Koenig, J.; Kirk, S. 2007. Woodsmoke Health Effects: A Review. *Inhal Toxicol* 19: 67-106. <https://doi.org/10.1080/08958370600985875>

Nascimento, A.P.; Santos, J.M.; Mill, J.G.; Toledo de Almeida Albuquerque, T.; Reis Júnior, N.C.; Reisen, V.A.; Pagel, É.C. 2020. Association between the incidence of acute respiratory diseases in children and ambient concentrations of SO₂, PM₁₀ and chemical elements in fine particles. *Environmental Research* 188: 109619. <https://doi.org/10.1016/j.envres.2020.109619>

- NIST. 2010.** *Chemistry Webbook*. Secretary of Commerce: United States of America. <http://webbook.nist.gov/chemistry>
- Olsen, Y.; Nøjgaard, J.K.; Olesen, H.R.; Brandt, J.; Sigsgaard, T.; Pryor, S.C.; Ancelet, T.; del Mar, M.; Querol, X.; Hertel, O. 2020.** Emissions and source allocation of carbonaceous air pollutants from wood stoves in developed countries: A review. *Atmospheric Pollution Research* 11(2): 234-251. <https://doi.org/10.1016/j.apr.2019.10.007>
- Oyarzún, M. 2010.** Contaminación aérea y sus efectos en la salud. *Revista Chilena de Enfermedades Respiratorias* 26(1): 16-25. <http://dx.doi.org/10.4067/S0717-73482010000100004>
- Ozil, F.; Tschamber, V.; Haas, F.; Trouvé, G. 2009.** Efficiency of catalytic processes for the reduction of CO and VOC emissions from wood combustion in domestic fireplaces. *Fuel Processing Technology* 90(9): 1053-1061. <https://doi.org/10.1016/j.fuproc.2009.03.019>
- Price-Allison, A.; Lea-Langton, A.R.; Mitchell, E.J.S.; Gudka, B.; Jones, J.M.; Mason, P.E.; Williams, A. 2019.** Emissions performance of high moisture wood fuels burned in a residential stove. *Fuel* 239: 1038-1045. <https://doi.org/10.1016/j.fuel.2018.11.090>
- Poláček, J.; Sitek, T.; Pospíšil, J.; Šnajdárek, L.; Lisý, M. 2021.** Emission of fine particles from residential combustion of wood: Comparison of automatic boiler, manual log feed stove and thermo-gravimetric analysis. *Journal of Cleaner Production* 279: e123664. <https://doi.org/10.1016/j.jclepro.2020.123664>
- Reyes, R.; Sanhueza, R.; Schueftan, A. 2020a.** Consumo de combustibles derivados de la madera en la región de O'Higgins: El desconocido rol de frutales y viñas en el abastecimiento regional de energía. *Bosque Energía Sociedad* 11. Instituto Forestal: Chile. 17p. <https://bibliotecadigital.infor.cl/handle/20.500.12220/29209>
- Reyes, R.; Sanhueza, R.; Schueftan, A. 2020b.** Consumo de leña y otros biocombustibles sólidos en la región de la Araucanía: nuevas cifras y tendencias. *Bosques Energía Sociedad* 12 Instituto Forestal: Chile. 24p. <https://bibliotecadigital.infor.cl/handle/20.500.12220/30392>
- Rinsky, R.A.; Smith, A.B.; Hornung, R.; Filloon, T.G.; Young, R.J.; Okun, A.H.; Landri-gan, P.J. 1987.** Benzene and leukemia. *The New England Journal of Medicine* 316(17): 1044-1050. <https://doi.org/10.1056/NEJM198704233161702>
- Radaideh, J. 2017.** Effect of Meteorological Variables on Air Pollutants Variation in Arid Climates. *Journal of Environmental and Analytical Toxicology* 7: 4. <https://doi.org/10.4172/2161-0525.1000478>
- Rokoff, L.; Koutrakis, P.; Garshick, E.; Karaga, M.; Oken, E.; Gold, D.; Fleisch, A. 2017.** Wood Stove Pollution in the Developed World: A Case to Raise Awareness Among pediatricians. *Current Problems in Pediatric and Adolescent Health Care* 47(6): 123-141. <https://doi.org/10.1016/j.cppeds.2017.04.001>
- Sáenz-Ceja, J.; Sáenz-Reyes, T.; Ríos, E. 2017.** Estufas ahorradoras de leña en la microcuenca Rosa de Castilla, Michoacán. *Revista Mitigación del Daño Ambiental Agroalimentario y Forestal de México* 3(3): 13-24. https://www.researchgate.net/publication/327881433_Estufas_ahorradoras_de_leña_en_la_microcuenca_Rosa_de_Castilla_Michoacan
- Satsangi, P.S.; Yadav, S.; Pipal, A.S.; Kumbhar, N. 2014.** Characteristics of trace metals in fine (PM_{2.5}) and inhalable (PM₁₀) particles and its health risk assessment along with in-silico approach in indoor environment of India. *Atmospheric Environment* 92: 384-393. <https://doi.org/10.1016/j.atmosenv.2014.04.047>
- Sinha, S.N.; Kulkarni, P.K.; Shah, S.H.; Desai, N.M.; Patel, G.M.; Mansuri, M.M.; Saiyed, H.N. 2006.** Environmental monitoring of benzene and toluene produced in indoor air due to combustion of solid biomass fuels. *Science of The Total Environment* 357(1-3): 280-287. <https://doi.org/10.1016/j.scitotenv.2005.08.011>
- SEC. 2020.** Establece valor del poder calorífico superior (pcs) para el combustible leña a usar en el cálculo de la potencia térmica nominal y eficiencia energética de los calefactores que utilizan dicho combustible. Ord N° 2266, 17/02/2015. Superintendencia de Electricidad y Combustibles: Santiago, Chile. <https://www.sec.cl/area-sec/organigrama-sec/>

Smith, K.R. 2000. National burden of disease in India from indoor air pollution. *Proceedings of the National Academy of Sciences of the United States of America* 97(24): 13286-13293. <https://doi.org/10.1073/pnas.97.24.13286>

Vicente, E.D.; Vicente, A.M.; Evtugina, M.; Oduber, F.I.; Amato, F.; Querol, X.; Alves, C. 2020. Impact of wood combustion on indoor air quality. *Science of The Total Environment* 705: e135769. <https://doi.org/10.1016/j.scitotenv.2019.135769>

Weinstein, J.; Diaz-Artiga, A.; Benowitz, N.; Thompson, L. 2020. Reductions in urinary metabolites of exposure to household air pollution in pregnant, rural Guatemalan women provided liquefied petroleum gas stoves. *Journal of Exposure Science & Environmental Epidemiology* 30: 362-373. <https://doi.org/10.1038/s41370-019-0163-0>

Wöhler, M.; Andersen, J.S.; Becker, G.; Persson, H.; Reichert, G.; Schön, C.; Schmidl, C.; Jaeger, D.; Pelz, S. 2016. Investigation of real life operation of biomass room heating appliances - Results of a European survey. *Applied Energy* 169: 240-249. <https://doi.org/10.1016/j.apenergy.2016.01.119>

Wolkoff, P. 1998. Impact of air velocity, temperature, humidity, and air on long-term voc emissions from building products. *Atmospheric Environment* 32(14-15): 2659-2668. [https://doi.org/10.1016/S1352-2310\(97\)00402-0](https://doi.org/10.1016/S1352-2310(97)00402-0)

Wu, C.F.; Wu, S.Y.; Wu, Y.H.; Cullen, A.C.; Larson, T.V.; Williamson, J.; Liu, L.J.S. 2009. Cancer risk assessment of selected hazardous air pollutants in Seattle. *Environment International* 35(3): 516-522. <https://doi.org/10.1016/j.envint.2008.09.009>

Zhou, C.; Zhan, Y.; Chen, S.; Xia, M.; Ronda, C.; Sun, M.; Shen, X. 2017. Combined effects of temperature and humidity on indoor VOCs pollution: Intercity comparison. *Building and Environment* 121: 26-34. <https://doi.org/10.1016/j.buildenv.2017.04.013>