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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

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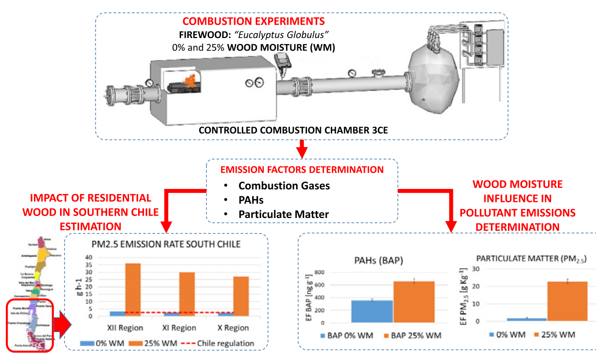
HIGHLIGHTS

- Optimization of combustion parameters for *Eucalyptus* was made on the new 3CE.
- Analytical methodology was optimized for determining PAHs in $PM_{2.5}$ from firewood.
- Reproducibility and repeatability to 16 EPA-PAHs determination in 3CE were studied.
- Effects at 0 and 25%WM on the EF of pollutants from *Eucalyptus* were determined.
- PM2.5 impact of residential wood combustion was evaluated in the south of Chile.

GRAPHICAL ABSTRACT



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ABSTRACT

Polycyclic aromatic hydrocarbons, $PM_{2.5}$ and micrometer-sized particles are mainly emitted by residential wood combustion, affecting air pollution in the cities of Chile. *Eucalyptus globulus* (EG) at 0% and 25% wood moisture was burning using a new controlled combustion chamber for emissions (3CE) to determine the emission factors of $PM_{2.5}$, micrometer-sized particle numbers (0.265 μm to 34.00 μm) and 16 EPA-PAHs plus retene adsorbed on $PM_{2.5}$ quartz filters. A method using accelerated solvent extraction, concentration, clean-up and GC–MS is proposed for determining emission factors for 16 EPA-PAHs for the concentration from biomass combustion. Chromatographic conditions and analytical steps were optimized in terms of linearity, selectivity, limits of detection and quantification, precision and accuracy. The recovery obtained from urban dust SRM 1649A (NIST reference material) analyses was between 63% (benzo[*b*]fluoranthene) and 102% (benzo[*k*]fluoranthene). In this investigation, it was shown that increasing the wood moisture in combustion tests decreased combustion efficiency (93% to 49%) and increased the emission factors of total PAHs (5215.47 ng g^{-1} to 7644.48 ng g^{-1}), the gravimetric PM2.5 (2.01 g kg^{-1} to 22.90 g kg^{-1}) and the total number of measured micrometer-sized particles (3.15 × 1012 particles kg^{-1} to 1.33 × 1013 particles kg^{-1}) due to incomplete combustion. The $PM_{2.5}$ emission rates (ERs) were estimated using EG at 0% WM (2.39 g $^{-1}$ to 3.15 gh^{-1}) and 25% WM (27.32 g h^{-1} to

Abbreviations: PAHs, polycyclic aromatic hydrocarbons; EFs, emission factors; EG, *Eucalyptus globulus*; RWC, residential wood combustion; WM, wood moisture; SEP, stage emission process; OPC, optical particulate counter; CE, combustion efficiency; 3 CE, controlled combustion chamber for emissions; ASE, accelerated solvent extraction; GC–MS, gas chromatography-mass spectrometry; AOA, atmospheric organic aerosol.

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35.77 g h^{-1}) for three regions of Chile. In almost all regions, the Chilean emission regulations were exceeded for $PM_{2.5}$ from wood combustion in the heater (stove with thermal power ≤8 kW and emission limit of 2.5 g h^{-1}). Finally, when using wet wood for residential combustion, the amount of PAHs on the $PM_{2.5}$ increased, presenting a potential hazard to population health. Therefore, improvements are necessary in the current regulation of PM emissions.

1. Introduction

In Chile, firewood is largely consumed as a primary energy source, being the second most important source of energy after petroleum (Ministry of Environment, 2011; Ministry of the Energy, 2015), with 59% of the consumption of firewood used for domestic heating stoves (chimneys and fireplaces) and wood-burning cook stoves. Wood burning generates a great amount of air pollutants ($PM_{1.0}$, $PM_{2.5}$, PM_{10}, atmospheric organic aerosols (AOA), and polycyclic aromatic hydrocarbons (PAHs), among others), mainly affecting the cities of central-south Chile (Rancagua, Talca, Curicó, Linares, Los Angeles, Concepción, Temuco, Osorno, Valdivia, Coyhaique) (Díaz-Robles et al., 2008, 2014).

Most of the research on air quality in Chile is focused on the emission of particles ($PM_{2.5}$ and PM_{10}) from residential wood combustion (RWC) (Pozo et al., 2015; Sanhueza et al., 2006; Kavouras et al., 2001). For example, Sanhueza et al. (2009) reported a strong relationship between daily mortality cases (1997–2002) among subjects aged 65 years old and PM_{10} in Temuco city. However, to complete such research, the chemical composition of atmospheric particulate matter must be known, especially toxic species such as PAHs, which are carcinogenic and mutagenic compounds (Mumtaz and George, 1996). Most PAHs (70–90%) are adsorbed on micrometre-diameter particle matter surfaces (inhalable particles). These particles can be deposited on the respiratory tract and thus increase the occurrence of adverse health effects. (Pope III, 2000; O'Neill et al., 2005; IARC, 2010; Kim et al., 2013). For these reasons, it is necessary to determine the emission factors (EFs) of atmospheric pollutants generated by RWC. An EF is defined as the mass of targeted pollutants emitted per unit mass of fuel burned or per unit of energy produced (Vicente and Alves, 2018). By identifying EFs as pollutants generated from RWC, it is possible to create more accurate emissions inventories (EIs), which allow for an estimation of the real impact of a given pollution source on urban air quality, on population health and on climate change (Cereceda-Balic et al., 2017).

Previous studies have reported EFs for different atmospheric pollutants (PM_{10}, $PM_{2.5}$, PAHs, methoxyphenols, resin acids, monosaccharide anhydrides, and inorganic compounds, among others) emitted by RWC (Alves et al., 2011; Fine et al., 2002; Fine et al., 2004a; Fine et al., 2004b; Gonçalves et al., 2010; Gonçalves et al., 2011; Hays et al., 2002; Hellén et al., 2008; Jimenez et al., 2017; McDonald et al., 2000; Nel, 2005; Simoneit and Elias, 2000; Vicente et al., 2016). For more detail, PAHs EFs are summarized in Table S.1., all of which have been determined by different analytical methods, for example, Soxhlet extraction (SOX) (Boman et al., 2011; Orecchio et al., 2016; Talebi and Taebi, 2004; Shen et al., 2012), a microwave-accelerated system (MAE) (Shen et al., 2012), refluxing (Gonçalves et al., 2010, 2011), accelerated solvent extraction (ASE) (Talebi and Taebi, 2004; Vicente et al., 2016), supercritical fluid extraction (SPE) (Talebi and Taebi, 2004) and ultrasound-assisted extraction (UAE) (Bignal et al., 2008; Riva et al., 2011). All research listed in the table used gas chromatography – mass spectrometry (GC–MS) because this method has proven to be an excellent analytical technique for analysing PAHs associated with particle and gas phase determination, with low detection limits. In the study by Jimenez et al. (2017), dry *Eucalyptus globulus* was burned in a single-chamber slow-combustion wood stove, where the PAH EFs of the sums of 12 PAHs in the particle phase were 1472.5 ng g^{-1}. Gonçalves et al. (2012), reported that the emission factors of wood burners for the sums of 11 PAHs in particle phases during the combustion of eucalyptus wood in both a fireplace and wood stove were 1349 ng g^{-1} and 7318 ng g^{-1}, respectively. In general, the differences between EFs are usually affected by several factors such as combustion technology (wood stove, fireplace, chimney, boilers), operating parameters (temperature, oxygen availability, and sampling procedure, among others) and fuel properties (fuel type and wood moisture) (McDonald et al., 2000; Orasche et al., 2013; Yang et al., 2017).

Chilean Standard (NCH 2907/2005, 2005) considers wood as a suitable material for RWC when the wood moisture (WM) content is less than or equal to 25%. For this reason, it is necessary to test the Chilean Standard considering that the influence of WM significantly affects pollutant emissions, as reported by researchers (Bignal et al., 2008; Chomanee et al., 2009 and Shen et al., 2012a, 2012b). EFs obtained for PM, organic compounds (OC) and PAHs increased with increasing WM. It was thought that when burning high-moisture fuel, extra energy is required to vaporize water, which usually results in reduced fuel combustion efficiency and increased emissions of pollutants from the incomplete combustion of wood (Rogge et al., 1998; Shen et al., 2013; Simoneit, 2002).

In this scenario, it is very important to evaluate the WM as the only variable to study in order to attribute its real effects on the emission of atmospheric pollutants, setting as constant the other operating parameters. Therefore, the objective of this research is to evaluate the influence of wood moisture on wood combustion and the resulting emissions of $PM_{2.5}$, PAHs and micrometer-sized particle numbers using one of the most commonly used woods in Chile (*Eucalyptus globulus*) at two different humidities: the first being 0% (the lower limit according to NCH 2907/2005 (2005)) and the second being 25% WM (the maximum limit according to NCH 2907/2005 (2005)). All these combustion tests were developed in the controlled combustion chamber of emissions (3CE, Chilean patent N° 843–2008, US13/977,825 Patent N° US9,791,151 B2, 2017; Patent application EP 20100861353.0, PCT/CL 00058, 12/30/2010, patent pending, Cereceda-Balic et al., 2017), an instrument that enables the controlling of all combustion parameters (flow and quality of oxidant, combustion chamber temperature, wood ignition procedure, air humidity, and more) using an optimized method for the sampling system.

2. Material and methods

2.1. Combustion tests and sampling system

Chilean forest plantations cover a total area of 3,046,904 ha, of which 64% corresponds to *Pinus radiata* species and 24% corresponds to *Eucalyptus globulus* (EG); however, EG is the most used species for RWC (Ministry of the Energy, 2015). For this reason, in this study, EG was used to perform all the combustion tests. Wood samples were obtained from local certified distributors. Then, wood was transported separately to the laboratory in sealed and appropriately labelled plastic containers appropriately. Once in the laboratory, wood samples were defined via granulometry and humidity (0% and 25%), and the emissions were analysed from of the gases and particles accumulated in the collection system of 3CE using the same methodology described by Cereceda-Balic et al., 2017.