Science of the Total Environment 612 (2018) 636–648

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Chemical composition and speciation of particulate organic matter from modern residential small-scale wood combustion appliances

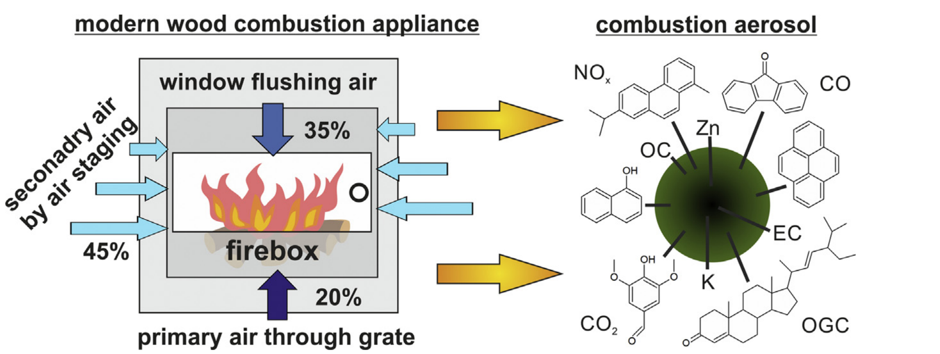
Hendryk Czech [a], Toni Miersch [a], Jürgen Orasche [a,b,c], Gülcin Abbaszade [b,c], Olli Sippula [c,d], Jarkko Tissari [d], Bernhard Michalke [e], Jürgen Schnelle-Kreis [b,c], Thorsten Streibel [a,b,c,⁎], Jorma Jokiniemi [c,d], Ralf Zimmermann [a,b,c]

[a] Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, Institute of Chemistry, University of Rostock, 18059 Rostock, Germany
[b] Joint Mass Spectrometry Centre, Cooperation Group "Comprehensive Molecular Analytics" (CMA), Helmholtz Zentrum München – German Research Centre for Environmental Health, 85764 Neuherberg, Germany
[c] Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE), Germany
[d] Fine Particle and Aerosol Technology Laboratory, Department of Environmental and Biological Sciences, University of Eastern Finland, FIN-70211 Kuopio, Finland
[e] Research Unit Analytical BioGeochemistry, Helmholtz Zentrum München – German Research Centre for Environmental Health, 85764 Neuherberg, Germany

HIGHLIGHTS

- PM2.5 composition from two modern wood combustion appliances
- Advanced targeted and non-targeted mass spectrometric techniques
- Emission factors for >100 organic particle constituents
- Low abundance of established wood combustion markers
- Slow ignition can shift emission pattern compared to regular combustion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 June 2017
Received in revised form 23 August 2017
Accepted 26 August 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Diagnostic ratios
Wood smoke
PAH
OPAH
Phenolics
Photoionisation mass spectrometry

ABSTRACT

Combustion technologies of small-scale wood combustion appliances are continuously developed decrease emissions of various pollutants and increase energy conversion. One strategy to reduce emissions is the implementation of air staging technology in secondary air supply, which became an established technique for modern wood combustion appliances. On that account, emissions from a modern masonry heater fuelled with three types of common logwood (beech, birch and spruce) and a modern pellet boiler fuelled with commercial softwood pellets were investigated, which refer to representative combustion appliances in northern Europe In particular, emphasis was put on the organic constituents of PM2.5, including polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (OPAHs) and phenolic species, by targeted and non-targeted mass spectrometric analysis techniques. Compared to conventional wood stoves and pellet boilers, organic emissions from the modern appliances were reduced by at least one order of magnitude, but to a different extent for single species. Hence, characteristic ratios of emission constituents and emission profiles for wood combustion identification and speciation do not hold for this type of advanced combustion technology. Additionally, an overall substantial reduction of typical wood combustion markers, such as phenolic species and anhydrous sugars, were observed. Finally, it was found that slow ignition of log woods changes the distribution of characteristic resin acids and phytosterols as

⁎ Corresponding author at: Joint Mass Spectrometry Centre, Chair of Analytical Chemistry, University of Rostock, 18059 Rostock, Germany.

http://dx.doi.org/10.1016/j.scitotenv.2017.08.263

well as their thermal alteration products, which are used as markers for specific wood types. Our results should be considered for wood combustion identification in positive matrix factorisation or chemical mass balance in northern Europe.

1. Introduction

In many countries of Europe as well as in North America, the residential combustion of biomass, in particular wood, as a renewable energy source is encouraged by legislation to decrease the dependence on fossil fuels and contribution to global warming. Conventional logwood stoves, pellet stoves and pellet boilers have been recognised to be substantial emitters of greenhouse gases, black or elemental carbon and brown carbon (Evtyugina et al., 2014; Martinsson et al., 2015; Orasche et al., 2012), which counteract the widely considered CO_2-neutrality and thus affect the climate (Andreae and Ramanathan, 2013). Furthermore, residential wood burning causes elevated ambient concentrations of inhalable particulate matter (PM) with an aerodynamic diameter below 2.5 μm (PM2.5) (Fuller et al., 2013), which has been associated with toxicological responses, such as genotoxicity, cytotoxicity, oxidative stress, systemic inflammation and cardiovascular diseases (Croft et al., 2017; Miljevic et al., 2010; Naeher et al., 2007; Sehlstedt et al., 2010). Also, the emissions of volatile organic compounds (VOCs) from wood combustion cover a substantial potential for secondary organic aerosol (SOA) formation (Bruns et al., 2016), which may have different health effects than the primary emissions (Künzi et al., 2013; Nordin et al., 2015) and additionally contributes to ambient PM2.5 levels.

In order to tackle these emissions, new and more complete combustion technologies were developed which may significantly reduce the toxicity potential of primary wood combustion aerosols (Jalava et al., 2012). Secondary air supply through air staging became an established emission abatement strategy, which substantial reduce the emissions of several organic and inorganic pollutants (Nuutinen et al., 2014). Air staging is characterised by splitting the total combustion air into under-stoichiometric air-to-fuel ratios for primary air ($\lambda < 1$) and consecutive addition of low excess secondary air ($\lambda > 1.5$), which is well-mixed with the pyrolysis gases through different feedings. Thus, high temperatures and more complete combustion are achieved (Nussbaumer, 2003). However, some pollutants correlate inversely with increasing secondary air flow rates, such as the trade-off between CO and NO_x (Khodaei et al., 2017).

Emissions from a masonry heater and a pellet boiler, equipped with air staging technology, were previously investigated regarding PM, CO, NO_x ($NO + NO_2$), total VOC (Lamberg et al., 2011a; Lamberg et al., 2011b; Nuutinen et al., 2014) and VOC composition (Czech et al., 2017; Czech et al., 2016; Reda et al., 2015), as well as their SOA formation potential (Kari et al., 2017; Tiitta et al., 2016). In this study, an additional detailed characterisation of the PM2.5 composition is presented with emphasis on the organic constituents, whose emission factors (EFs) are compared to conventional and other modern wood stoves. The implications for source apportionment studies of the results on chemical patterns of emissions are also discussed, especially the implications for selecting common diagnostic ratios to trace sources and quantify source contributions from biomass burning to ambient PM concentrations. Moreover, differences of EFs and emission profiles between wood types are related to effects observed in toxicological studies (Kasurinen et al., 2017).

Although the masonry heater and the pellet boiler of this study are only representative domestic combustion appliances in northern Europe, it was pointed out that especially features of regional emission activity are important for emission inventories and source apportionment (Hellén et al., 2008; Pastorello et al., 2011). In the end, the EFs from the two combustion appliances can be also involved in simulations of future emission scenarios to estimate benefits of emission abatement technologies on air quality (Fountoukis et al., 2014).

2. Material and methods

2.1. Experimental setup

2.1.1. Combustion appliances

The emissions of two small-scale wood combustion appliances with advanced secondary air supply for residential heating were investigated. The modern masonry heater (*Hiisi 4*, Tulikivi Ltd., Finland) comprises of a massive soap stone of app. 1.3 tons for slow heat release, an upright enclosed firebox and a double glass window door. In the firebox, the secondary air is supplied through panels with small rifts in the upper combustion chamber (air staging) to generate a secondary combustion zone, which was shown to substantially reduce emissions of CO, VOCs and organic matter (Nuutinen et al., 2014). The modern masonry heater was operated at approximate nominal load.

The second appliance is an automatically-fired top-feed pellet boiler (*PZ25RL*, Biotech Energietechnik GmbH, Austria), which was continuously operated at its nominal power of 25 kW. A more detailed description of the pellet boiler and the effect of air staging can be found in Lamberg et al. (2011b).

In the following, the term "modern" refers to wood combustion appliances with air staging and "conventional" without.

This study was part of experiments by Helmholtz Virtual Institute of Complex Molecular System in Environmental Health (HICE), which aims to explore biological effects of emissions on human lung epithelial cells (Kanashova et al., 2017). In particular, emissions from state-of-the-art combustion appliances and emerging fuels are of interest as they may represent future scenarios. The two combustion appliances were chosen due to their known low emissions of bulk components from previous studies (Nuutinen et al., 2014; Lamberg et al., 2011b) and their representativeness for single houses in terms of energy output and market availability.

2.1.2. Fuels and combustion procedure

The modern masonry heater was fuelled by beech (*Fagus sylvatica*) and spruce (*Picea abies*), which are common firewood in central Europe, as well as birch (*Betula pubescens*), which is a typical firewood in northern Europe. In Table 1, physico-chemical properties of the three types of firewood are summarised. In total 15 kg of logwood was burned in a single experiment, split up in six consecutive batches of 2.5 kg each. The ignition of the first batch in the cold stove was carried out from top down with 150 g of small wood sticks/chips. After 35 min, the next batch was put in the wood combustion residues for self-ignition and burned for further 35 min. Subsequent to the sixth batch, remaining ember was stoked and the secondary air supply was blocked according to manufacture instructions for 30 min to cover a total experimental time of 4 h.

In two (spruce* and birch*) of the total log wood combustion experiments, a slow ignition of the first batch was observed. Due to qualitative and quantitative differences in emissions of these experiments compared to the other ones, the effect of slow ignition on the total EFs is discussed more in detail in Section 3.5.

The pellet boiler was operated with commercial softwood pellets (produced from pine and spruce stem wood, physico-chemical properties in Table 1) under stable conditions over 4 h and connected to a heat exchanger. Those boilers are usually connected to a reservoir of water for