Atmospheric Environment 45 (2011) 4533–4545

Contents lists available at ScienceDirect

Atmospheric Environment

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

Organic compounds in $PM_{2.5}$ emitted from fireplace and woodstove combustion of typical Portuguese wood species

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ARTICLE INFO

Article history:
Received 14 February 2011
Received in revised form
25 May 2011
Accepted 27 May 2011

Keywords:
Biomass burning
Fireplace
Woodstove
$PM_{2.5}$
GC–MS
Organic tracers

ABSTRACT

The aim of this study is the further characterisation of $PM_{2.5}$ emissions from the residential wood combustion of common woods grown in Portugal. This new research extends to eight the number of biomass fuels studied and tries to understand the differences that the burning appliance (fireplace versus woodstove) and the combustion temperature (cold and hot start) have on emissions. *Pinus pinaster* (Maritime pine), *Eucalyptus globulus* (eucalypt), *Quercus suber* (cork oak), *Acacia longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (Olive), *Quercus ilex rotundifolia* (Holm oak) and briquettes produced from forest biomass waste were used in the combustion tests. Determinations included fine particle emission factors, carbonaceous content (OC and EC) by a thermal–optical transmission technique and detailed identification and quantification of organic compounds by gas chromatography–mass spectrometry. Fine particle emission factors from the woodstove were lower than those from the fireplace. For both combustion appliances, the OC/EC ratio was higher in "cold start" tests (1.56 ± 0.95 for woodstove and 2.03 ± 1.34 for fireplace). These "cold start" OC/EC values were, respectively, for the woodstove and the fireplace, 51% and 69% higher than those obtained in "hot start" experiments. The chromatographically resolved organics included *n*-alkanes, *n*-alkenes, PAHs, *n*-alkanals, ketones, *n*-alkanols, terpenoids, triterpenoids, phenolic compounds, phytosterols, alcohols, *n*-alkanoic acids, *n*-di-acids, unsaturated acids and alkyl esters of acids. The smoke emission rate and composition varied widely depending on fuel type, burning appliance and combustion temperature.

1. Introduction

Residential wood log combustion is considered to be a major emission source of local and regional air pollution, especially for particulate matter and hydrocarbons, such as polycyclic aromatics (Fine et al., 2004b; Rogge et al., 1998; Schmidl et al., 2008a). The flue gases from residential biomass combustion are dominated by submicron particles (<1 μm) by number and often also by mass, and there is an increasing interest in their characteristics and implications to human health (Lighty et al., 2000). Besides the health-related implications, these aerosols have climate-forcing impacts, either contributing to, or balancing, the effects of greenhouse gases (Danny and Kaufmann, 2002). In Europe, emissions from biomass combustion are one of the major sources of atmospheric aerosol mass during winter (Puxbaum et al., 2007; Gelencsér et al., 2007). Modelling results showed that in Portugal 18% of PM_{10} could be related to this emission source, which may deeply impact the levels in the atmosphere (Borrego et al., 2010). Source apportionment of $PM_{2.5}$ aerosol applied to ambient measurements in a coastal/rural area in Portugal showed that 52–69% of the organic carbon is assigned to residential wood burning for heating (Gelencsér et al., 2007). Responses to a national survey (unpublished data) indicated that, on average, 34% of the Portuguese population uses residential wood combustion for heating purposes, but this percentage can reach 62% in cold inland districts, such as Viseu. In Portugal and other Mediterranean countries, there is a lack of information concerning the characteristics of particulate emissions from biomass combustion systems. Emission inventories and source apportionment studies (e.g. Caseiro et al., 2009; Kupiainen and Limonet, 2007; Yin et al., 2010) have been using default values obtained for United States (e.g. Fine et al., 2004a,b), mid-European Alpine region (Schmidl et al., 2008a), or Scandinavian (Hedberg et al., 2002; Johansson et al., 2004) biofuels, uncommon in Southern Europe. Because of the lack of biomass burning profiles for Southern Europe, positive matrix factorisation or principal components analysis (unknown sources)

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doi:10.1016/j.atmosenv.2011.05.071

instead of chemical mass balance (known sources) have been used to apportion different inputs to the ambient aerosol (e.g. Callen et al., 2009). To overcome the lack of information, a series of source tests were made to evaluate the chemical composition of particulate matter (PM_{10}) emissions from the woodstove combustion of four prevalent Portuguese species of wood: *Pinus pinaster*, *Eucalyptus globulus*, *Quercus suber* and *Acacia longifolia*. The burning tests were carried out at the combustion facility of the Vienna University of Technology, on a highly efficient "chimney type" log woodstove and the results were published by Gonçalves et al. (2010). The objectives of this new investigation are to extend to eight the number of biomass fuels studied and try to understand the effects of traditional Portuguese burning appliances (a brick open fireplace versus a cast iron woodstove) and combustion conditions on emissions. In addition to a larger number of wood species involved in the present study in comparison to that in Gonçalves et al. (2010), the two major differences between both investigations are related to the use of burning appliances with distinct characteristics ("chimney type" stove in Austria with high efficiency versus traditional Portuguese equipments with lower efficiency) and sampling of particulate matter with distinct aerodynamic diameters (PM_{10} for the Austrian stove, $PM_{2.5}$ for the Portuguese appliances).

Characterisation of the emissions for different types of appliances during different operation conditions (cold and hot start phases) makes it possible to identify when the major parts of the emissions occur and actions for emission reduction can then be achieved where the savings can be highest. On the other hand, by weighting the source test results in proportion to the availability of firewood from specific tree species, the quantities of wood burned in each region, type and number of household burning appliances, and prevailing combustion conditions in "ordinary" domestic operation, it will be possible to develop composite regional source profiles for Chemical Mass Balance receptor models, to account for particulate organic emissions at a country-scale and to quantify the regional differences in wood smoke composition.

2. Experimental work

2.1. Biomass fuel selection

According to the Portuguese Forest Inventory (2005), the top seven nationally predominant tree species are *P. pinaster* (Maritime pine), *E. globulus* (Eucalypt), *Q. suber* (Cork oak), *A. longifolia* (Golden wattle), *Quercus faginea* (Portuguese oak), *Olea europea* (olive) and *Quercus ilex rotundifolia* (Holm oak). The burning emissions of all these species were studied and results are presented here. In addition, biomass briquettes made of wastes from forest cleaning activities and/or wastes from local wood processing industries, common in home heating nowadays, were also studied and evaluated. The elemental composition, ash and moisture content of all tested fuels are presented in Table 1.

Table 1
Elemental composition, ash and moisture content of biofuels (% w/w).

Biomass	% Moisture content	Elemental composition (dry basis)					Ashes
		C	H	N	S	O (by difference)	
Maritime pine	9.10	51.4	6.20	0.160	n/d	41.9	0.360
Eucalypt	11.3	48.6	6.20	0.160	n/d	44.3	0.750
Cork oak	12.2	51.6	6.03	0.180	n/d	40.8	1.41
Olive	15.5	53.6	7.68	0.180	n/d	36.6	1.94
Portuguese oak	14.1	50.3	7.32	0.190	n/d	41.8	0.380
Holm oak	8.70	50.6	7.14	0.180	n/d	39.7	2.32
Golden wattle	8.40	50.8	6.43	0.180	n/d	41.8	0.750
Briquettes	8.40	50.8	7.01	0.160	n/d	41.2	0.910

n/d – not determined because the concentration level was below detection level of 0.01% w/w.

2.2. Sampling details

The burning tests were carried out at the Department of Environment, University of Aveiro, combustion facility. The facility structure and operational conditions were described in detail by Fernandes (2009). Two types of residential biomass combustion appliances were selected for the source tests: i) a cast iron woodstove (Solzaima, model Sahara), operated manually in batch mode with handheld control of combustion air, and ii) a traditional Portuguese brick open fireplace operated manually in batch mode and with no control of combustion air. In order to evaluate the influence of the temperature and fuel ignition process on the combustion flue emission characteristics, two sets of experiments were performed for each appliance and wood fuel type: cold start and hot start. In the experiments with cold start, the combustion began with the appliance at ambient temperature. Thus, the "cold start" experiments represent the post-ignition combustion phase. The hot start experiments were initiated with the load of a batch of fuel to the combustion chamber already at a temperature of around 100 °C and with the presence of a small amount of burning char from a batch of fuel already burned previously. The continuous monitoring of temperatures was made with K-type thermocouples in the middle point of each combustion chamber. The temperature in the combustion chamber of the fireplace, on average, was 128 °C $\pm$ 66 °C for "cold start" and 179 °C $\pm$ 63 °C for "hot start". The temperature in the combustion chamber of the woodstove, on average, was 248 °C $\pm$ 69 °C for "cold start" and 307 °C $\pm$ 67 °C for "hot start". It should be noted that Tiegs (1995) reported that the cold start-up PM emissions can be about half of the emissions from a full combustion cycle. Thus, emissions from different combustion phases should be accounted for in order to develop composite emission profiles for further application in source apportionment methodologies.

The wood was cut into logs of 30–40 cm in length. Before each burning test, a batch of dry wood was weighed in a balance. The weights ranged between 1.9 and 2.2 kg. The ignition of the wood was achieved using small pieces cut from the same wood being burned. Burn times ranged from 45 to 90 min. Particle sampling began immediately prior to ignition and was ceased at the end of combustion. Collection of particulate matter with aerodynamic diameters below 2.5 μm ($PM_{2.5}$) was performed in a dilution tunnel. Dilution sampling is used to characterise particle emissions from combustion because it simulates the rapid cooling and dilution that occurs as exhaust mixes with the atmosphere (Lipsky and Robinson, 2005). The dilution tunnel consisted of a cylindrical tube with 0.20 m internal diameter and 11 m length. The sampling of $PM_{2.5}$ was made at a dilution ratio of 25:1. $PM_{2.5}$ were collected using an Echo sampling head connected to a TECORA sampler (model 2.004.01, Italy) operating at a flow of 2.3 $m^3 h^{-1}$, onto quartz fibre filters (47 mm diameter), located at 10 m downstream the dilution tunnel entering. The temperature in the particle sampling point in the dilution tunnel was in the range 25–35 °C.

After each combustion experiment, the $PM_{2.5}$ sampling head was cleaned to minimise contamination of the subsequent experiments. Background samples were collected to assess any contamination arising from the dilution air; negligible levels of particulate matter, organic carbon and elemental carbon were found. The conditions at the exit of the chimney of the woodstove or fireplace are different from those in the dilution tunnel. For this reason, the $PM_{2.5}$ concentrations at the exit of the chimney were