

ANALYSIS OF THE CHEMICAL COMPOSITION OF ULTRAFINE PARTICLES FROM TWO DOMESTIC SOLID BIOMASS FIRED ROOM HEATERS UNDER SIMULATED REAL-WORLD USE

Senem Ozgen (1), Silvia Becagli (2), Vera Bernardoni (3), Stefano Caserini (1), Donatella Caruso (6), Lorenza Corbella (4), Manuela Dell'Acqua (3), Paola Fermo (4), Raquel Gonzalez (4), Giovanni Lonati (1), Stefano Signorini (5), Ruggero Tardivo (1), Elisa Tosi (1), Gianluigi Valli (3), Roberta Vecchi (3), Marina Marinovich (6)

(1) Department of Civil and Environmental Engineering, Politecnico di Milano, Milan, 20133, Italy, phone: +39 0223996430 (2) Department of Chemistry, Università degli Studi di Firenze, (3) Department of Physics, Università degli Studi di Milano and INFN - Milano, (4) Department of Chemistry, Università degli Studi di Milano, (5) Energy and Environment Laboratory (LEAP) Piacenza, Piacenza, (6) Department of Pharmacological and Biomolecular Sciences, Università degli Studi di Milano.

ABSTRACT: Two common types of wood (beech and fir) were burned in commercial pellet (11.1 kW) and wood (8.2 kW) stoves following a combustion cycle simulating the behavior of a real-world user. Ultrafine particulate matter (UFP, $d_p < 100$ nm) was sampled with three parallel multistage impactors and analyzed for metals, main water soluble ions, anhydrosugars, total carbon, and PAH content. The measurement of the number concentration and size distribution was also performed by a fourth multistage impactor. UFP mass emission factors averaged to 424 mg/kg_{fuel} for all the tested stove and wood type (fir, beech) combinations except for beech log burning in the wood stove (838 mg/kg_{fuel}). Compositional differences were observed for pellets and wood UFP samples, where high TC levels characterize the wood log combustion and potassium salts are dominant in every pellet sample. Crucial aspects determining the UFP composition in the wood stove experiments are critical situations in terms of available oxygen (a lack or an excess of combustion air) and high temperatures. Whereas for the automatically controlled pellets stove local situations (e.g., hindered air-fuel mixing due to heaps of pellets on the burner pot) determine the emission levels and composition. Wood samples contain more potentially carcinogenic PAHs with respect to pellets samples. Some diagnostic ratios related to PAH isomers and anhydrosugars compiled from experimental UFP data in the present study and compared to literature values proposed for the emission source discrimination for atmospheric aerosol, extend the evaluation usually limited to higher particle size fractions also to UFP.

Keywords: ultrafine particle emission, chemical composition, small scale application, stove, wood pellet, wood.

1 INTRODUCTION

Currently residential wood combustion is increasing in Europe because of rising fossil fuel prices but also due to climate change mitigation policies. However, especially in small-scale applications, residential wood combustion may cause high emissions of particulate matter (PM) (Denier van der Gon et al., 2015).

Emissions from biomass burning are found to be mostly in the fine particle size fraction. Only minor fractions of the total PM mass correspond to diameters larger than 10 μm (Boman et al., 2004). The study of the size dependent response of particle emissions to variations in combustion conditions shows that UFP contribution to the measured mass relatively increases

11 under good operational practice with respect to the operation by restricting the combustion air
12 supply and slightly overloading the firebox with fuel (Leskinen et al., 2014; Lamberg et al.,
13 2011; Tissari et al., 2008). The particles are reported to contain sulfate, nitrate, chloride,
14 sodium, potassium, calcium, magnesium, ammonium, zinc, elemental carbon, and particulate
15 organic matter (Saarnio, 2013). Inorganic particles, mainly alkali salts, are formed from
16 volatilized fuel ash constituents, which condense either when the
17 temperature decreases or when chemical reactions form lower vapor pressure species
18 (Sippula, 2010). Incomplete combustion of organic compounds formed from the
19 decomposition due to heating of the biomass material and the consequent gas-to-particle
20 conversion (nucleation or condensation on other existing particles) under low-temperatures is
21 the source of organic content of the particles (Obaidullah et al., 2012). The origin of soot
22 particles are due to reactions of tar in the early fuel-rich regions in the flame and the low
23 temperatures in the combustion zone is a possible reason for lacking soot oxidation in the
24 fuel-lean region of the combustion chamber with consequent release with the flue gas
25 (Wiinikka et al., 2006). Specifically for UFP fraction, Tissari et al., (2008) found in particle
26 samples collected from a conventional masonry heater, UFP that were composed mainly of K,
27 S and Zn, and, to a lesser extent, of C, Ca, Fe, Mg, Cl, P and Na, while large agglomerates
28 contained mainly carbon (soot particles). Fernandes and Costa (2012) observed for a pine
29 pellet-fired boiler (22 kW) that UFP were composed mainly of O, K, Cl, Na and S, regardless
30 of the boiler operating condition. Similarly, Torvela et al. (2014) detected UFP mainly
31 composed of ash material in the emissions of a research biomass grate combustion unit (40
32 kW) combusting wood chips. Longhin et al., (2016) observed K, Mn and Ca in the UFP from
33 a modern pellet boiler (25kW). Park et al., (2013) analyzed water soluble components of PM
34 from the combustion of different biomass materials (agricultural and forest residues) and
35 found that the analyzed water soluble ions (e.g., organic, potassium, sulfate, chloride) showed
36 higher mass in the UFP fraction than the higher particle diameters.

37 Existing research efforts for providing emission factors for chemical species of the
38 particles from biomass combustion are mostly directed to characterize coarse ($d_p < 10 \mu\text{m}$),
39 fine ($d_p < 2.5 \mu\text{m}$) and submicron particle emissions (e.g., Vicente et al., 2015, Lamberg et al.,
40 2011 and many others). Differently from the above mentioned studies our study focuses on
41 the characterization of ultrafine particles (UFP, diameter $< 100 \text{ nm}$) that are indicated in
42 recent research to present a series of specific characteristics and reactivity patterns that differ
43 from that of larger particles (Diaz-Robles et al., 2014). Cassee et al. (2013) report in their
44 review the concern for particle sizes such as ultrafine particles and certain chemical-specific
45 constituents of PM such as sulfates, transition metals and polycyclic aromatic hydrocarbons
46 without a definite conclusion on the toxicity of the PM released from biomass combustion.
47 They reaffirm the need for further research to establish whether exposure to ultrafine particles
48 alone can substantially contribute to the adverse effects of PM.

49 The present work is a part of a larger project (TOBICUP - TOxicity of BIomass
50 COmbustion generated Ultrafine Particles) designed to gain deeper insight on the possible
51 negative toxicological effects of UFP. TOBICUP project aims to verify the toxicological
52 responses of the samples collected both directly from residential wood combustion emissions
53 under burning cycles reflecting real-life situations and in ambient air at a sampling site where
54 biomass burning for residential heating is widely used. Given the possible dependence of
55 toxicological responses on the physical-chemical properties of the particles, the main goal of
56 this study is the physical-chemical characterization of UFP from biomass burning in small-
57 scale appliances.

58 Our previous experience has shown the importance of capturing the emission
59 characteristics in the proximity of the source when the flue gas exiting the chimney is not
60 fully diluted and the particulate matter emissions have not yet completely undergone
61 oxidation by reactive atmospheric species (Ozgen et al., 2013). Taking into account the fact
62 that the limited emission height of domestic heating appliances may increase the exposure of
63 the population living nearby the source, the current study is designed also to reflect, as close

64 as possible, the changes in the emissions, enhancing the dynamic processes involving the
65 particles, exhausting the potential of the flue gas to condense upon further cooling.

67 **2 EXPERIMENTAL SECTION**

69 **2.1 Combustion appliances and test fuels**

70 Two commercial residential solid biomass room heaters (one automatically stoked and one
71 manually fed appliance) were tested in the Laboratory for Energy and Environment of
72 Piacenza, Italy (LEAP) facility (www.leap.polimi.it). Detailed information on the test fuels is
73 provided in the supplementary material (Table SM1).

74 Eight tests were performed with an 11.1 kW top-feed pellet stove. Pellets are fed from the
75 internal storage to the burner pot. The ignition occurs by means of an electric device. The
76 primary air is supplied from the bottom grate under the fuel bed and through the holes on
77 vertical walls in correspondence of the lowest part of the flame zone. The secondary air (i.e.,
78 window flush) enters through slits in the upper part of the front window. The air and fuel
79 supply rates are regulated automatically based on the stove heat output. Cleaning session is
80 performed automatically for 20 seconds every hour by injecting air from the bottom of the
81 burner pot. Five tests were conducted using wood pellets of class A1 (EN 17225-2:2014)
82 produced from 100%_w fir wood (moisture: 7%_w, ash: 0.3%_{w,dry}, S: 59 mg/kg_{dry}). Beech wood
83 pellets without class indication but with higher sulfur and ash content (moisture: 6.7%_w, ash:
84 1.2%_{w,dry}, S: 139 mg/kg_{dry}) were fed into the stove in the remaining three tests.

85 Seven tests were conducted on an 8.2 kW wood stove. The stove is made of steel with cast
86 iron grate and the firebox lined with heat-resistant ceramic. The stove operates with a state-of-
87 the-art triple combustion air supply. The primary air enters from the bottom of the grate, the
88 pre-heated window wash flow (the secondary air) enters at the top of the front window, and
89 finally the makeup air for combustion (the tertiary air) is supplied in the higher part of the
90 firebox to complete the combustion reactions. The test fuel (some of the logs with bark)
91 consisted of beech firewood (moisture: 11%_w, ash: 0.7%_{w,dry}, S: 101 mg/kg_{dry}) in four tests
92 and of fir wood (moisture: 10.7%_w, ash: 0.2%_{w,dry}, S: 56 mg/kg_{dry}) in the remaining three tests.

94 **2.2 Experimental details**

95 Previous experience have shown the increase of stove emissions when tested under
96 combustion cycles simulating the user behavior identified based on real-world field
97 experience with respect to combustion cycles under type-testing (Ozgen et al., 2014). The
98 present study followed a different approach in representing the real-world emissions: it aimed
99 to characterize the UFP emissions under burning conditions capturing the user behavior in
100 case the manufacturer instructions supplied with the stove (e.g., startup positioning of logs for
101 the initial batch, the control of the air valves) are followed.

102 For the pellets stove a burning cycle (3-4 hours, detailed information in Table SM2,
103 supplementary material) based on an operation with modulated-heat output was first
104 determined through preliminary tests taking into account the average heating demand of the
105 climatic zone where the tests were conducted (Lombardy Region, Northern Italy). The
106 appliance was operated about 55% of the time at 75% of its nominal load and the rest of the
107 run-time at the minimum load (about 30% of the nominal load). One test was conducted at
108 75% load without modulating. Sampling began when the stable operation conditions were
109 reached. The results include only the transitory periods for power modulation: the start up and
110 shut down periods are excluded. Despite no apparent mechanical problem in the pellet
111 conveyor or in the cleaning mechanism, some tests were characterized by heaps of ash and
112 unburnt pellet on the hopper.

113 For the wood stove, the burning cycle (5-7 hours, detailed information in Table SM2,
114 supplementary material) comprised the loading of four to five consecutive batches comprising
115 the cold start, eventual preheating period, two nominal loads and a final high load batch

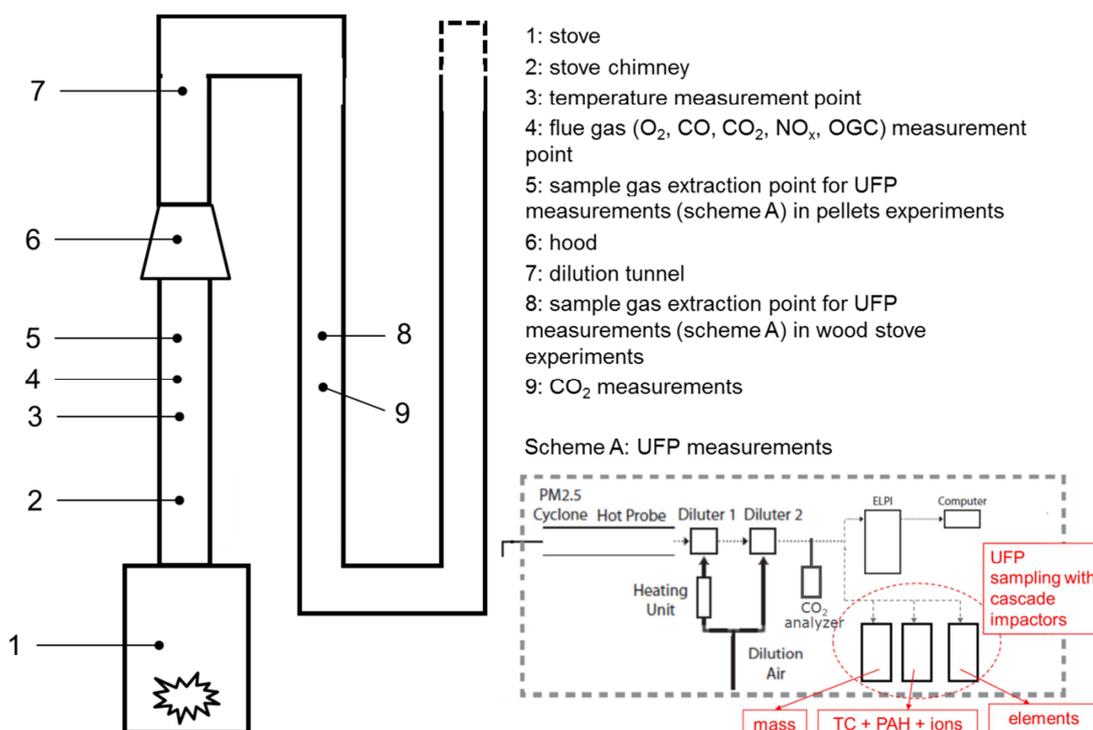
116 including the burn-out period. The start up batch consisted of small wood logs, fir wood sticks
 117 and of kerosene based fire starter. The initial batch was ignited from the top. During some
 118 tests the furnace was further preheated after the cold start with additional small batches.
 119 Afterwards, two batches of nominal load (about 2 kg/h, ~20 cm x ~11 cm x ~8 cm pieces)
 120 were loaded. The burning cycle was concluded with a higher load batch (about 1.3 times the
 121 nominal load) with slightly bigger logs. The start-up and loading procedure followed the
 122 prescriptions of the manufacturer. During loading of a new batch, the air control levers (both
 123 primary and secondary air) and the stove door were kept open for a lapse of time to permit the
 124 wood to catch fire, then the door was closed and the air control levers were set to nominal
 125 position. The unburned residues and inorganic ash were removed from the appliance and the
 126 firebox cleaned at the end of each test day.

127 The combustion appliances were set on a weigh-scale (readability 0.1 kg) to monitor the
 128 fuel consumption. The stove chimney was under a laboratory extraction system (i.e., dilution
 129 tunnel with the hood) which applied a continuous draft above the minimum draft
 130 recommended by the manufacturer (12 kPa).

131 For the pellets stove tests the flue gas was directly extracted (point 5 in Figure 1) from the
 132 chimney of the appliance and sent to the UFP sampling system (scheme A in Figure 1)
 133 described in section 2.3. While during the wood stove experiments, the flue gas was extracted
 134 from the dilution tunnel (point 7 in Figure 1) to further enhance the gas-to-particle conversion
 135 of the semi-volatile products of combustion. The average dilution ratio monitored in the
 136 dilution tunnel through simultaneous CO₂ measurements in the chimney and the tunnel, was
 137 about 16. The chimney gas was cooled and mixed with the indoor air upstream of the
 138 extractive sampling locations (point 8 in Figure 1), before being sent to the UFP sampling
 139 system (scheme A in Figure 1) described in section 2.3, the same as the one used for the
 140 pellets stove.

141 The gaseous compounds (CO, CO₂, organic gaseous compounds (OGC) divided in
 142 methane and non-methane hydrocarbons (NMHC), NO_x, O₂) and the flue gas temperature
 143 were also monitored throughout the testing period.

144



145

146

147 Figure 1: Experimental set up for residential solid fuel appliance testing

148

149 **2.3 UFP sampling and chemical characterization**

150 UFP samples were collected by means of three multistage cascade impactors in parallel.
151 Particle number size distribution was also performed by a fourth multistage cascade impactor
152 (Electrostatic low pressure impactor ELPI, Dekati). The impactors were positioned at the end
153 of the sampling line comprising a PM2.5 cyclone inlet, a heated probe and a two-stage diluter
154 (Fine particle sampler - FPS4000, Dekati). The total dilution ratios ranged between 90-150
155 corresponding to sample temperatures of 28°C-32°C during the pellet stove experiments and
156 400-1000 (including also the dilution tunnel) with sample temperatures of about 21°C-26°C in
157 the wood stove experiments.

158 For all multistage impactors, only the particles (aerodynamic diameter less than ~100nm)
159 collected on the two lower impaction stages and the back-up filter were sent to chemical
160 characterization and gravimetric analysis.

161 The multistage impactors operated on different substrates, depending on the subsequent
162 analysis to be performed. One of the impactors (Small Deposit Impactor SDI, Dekati, details
163 in Bernardoni et al., 2011) collected UFP on polycarbonate impaction stages and on PTFE
164 back-up filter for elemental analysis (all these substrates were also weighed for gravimetric
165 determination). The SDI has an effective cut-off diameter ($d_{p50\%}$) of 89.7 nm at the upper
166 stage considered for UFP determination. The other impactor (micro-orifice, uniform deposit
167 impactor MOUDI, MSP corporation) operated with quartz fiber filters: half of each filter was
168 devoted to the determination of ions, total carbon, and levoglucosan and its isomers, whereas
169 the other half was devoted to polycyclic aromatic hydrocarbons (PAH) analysis. Another
170 MOUDI impactor collected UFP (the upper stage considered has $d_{p50\%}$ of 95 nm) on
171 aluminum foils and a PTFE back-up filter for gravimetric determination and toxicological
172 tests (results not reported here). The UFP mass was determined from the aluminum foils and
173 PTFE filters gravimetrically using a microbalance (MX5 Mettler-Toledo, sensitivity 1 μ g)
174 located in a controlled weighing chamber ($T = 20 \pm 2^\circ\text{C}$ and $\text{RH} = 50 \pm 5\%$) where the filters
175 were conditioned for 48 h before weighing.

176 The physical-chemical UFP characterization comprised the detection of the following
177 species:

178 - total carbon (TC) \rightarrow TC analysis was performed by a TOT (Thermal Optical
179 Transmittance, Sunset Laboratory) instrument on a quartz fiber filter punch (1.5 cm^2) taken
180 from each filter, using analysis protocol NIOSH-870.

181 - water soluble ionic species (WSIS) \rightarrow 4.5 cm^2 of the three quartz fiber filters were put
182 together in a test tube and extracted with 5 mL of MQ water in an ultrasound bath for 1 hour.
183 Ion Chromatography (IC) has been employed for the quantification of the main ions.
184 Measurements of cationic (K^+ , Ca^{2+} , Na^+ , NH_4^+ , Mg^{2+}) and anionic (Cl^- , NO_2^- , NO_3^- , SO_4^{2-} ,
185 formate, acetate, propionate, oxalate) species were carried out using an ICS-1000 HPLC
186 system equipped with a conductivity system detector. Anion analysis was carried out with an
187 Ion Pac AS11 column using KOH from 1 to 17 mM, flow rate of 1 mL/min, for the detection
188 a conductivity system detector working with an anion self-regenerating suppressor AERS 500
189 was used. Cations determination was performed using a CS17 (Dionex) column and
190 methanesulfonic acid (MSA) from 0.5 to 10 mM as eluent at a flow rate of 0.25 mL/min and
191 for the detection a conductivity system equipped with a cation self-regenerating suppressor
192 CERS 500. (Piazzalunga et al., 2013)

193 - anhydrosugars (AS) \rightarrow the extraction from the quartz fiber filters followed the
194 methodology described for the water soluble ions. The analyses for levoglucosan and its
195 isomers were carried out by HPAEC-PAD using an ion chromatograph Dionex ICS1000.
196 Different anhydrosugars (i.e., levoglucosan, mannosan and galactosan) were separated using a
197 Carbowac PA-20 guard column and a Carbowac PA-20 anion exchange analytical column. As
198 eluent, NaOH 18 mM was used with a flow rate of 0.5 mL/min. An amperometric detector
199 (Dionex ED50) equipped with an electrochemical cell was used. (Piazzalunga et al., 2013)

200 - elements (ELM) \rightarrow Elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Sr, Ti,
201 V, Zn) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-
202 AES) (Varian 720-ES). Solubilization procedure followed the EN14902:2005 methodology

203 by using concentrate sub-boiled distilled HNO₃ and 30% ultrapure H₂O₂ in a microwave oven,
204 at 220°C for 25 min (P= 55 bar) (Perrone et al., 2013).

205 - polycyclic aromatic hydrocarbons (PAH) → Eight PAHs (3-ring isomers with molecular
206 weight (MW) 178: phenanthrene [Phe], anthracene [Ant], 4-ring isomers with MW 202:
207 fluoranthene [Flu], pyrene [Pyr], 4-ring isomers with MW 228: benzo(a)anthracene [BaA],
208 chrysene [Cry], 5-ring isomers with MW 252: benzo(b)fluoranthene [BbF], benzo(a)pyrene
209 [BaP]) were evaluated by gas chromatography-mass spectrometry (GC-MS Varian 2100T
210 equipped with a Electron Ionization source). Samples were weighted, add with internal
211 standards (100 ng/sample) ¹²D Benzo(α)anthracene and ¹²D Chrysene, transferred into tube
212 with 7 ml of dichloromethane, vortexed for 1 min and dried under nitrogen flow. After
213 resuspension with 5 ml of acetonitrile, the organic portion were filtered using syringe with
214 filter RC 0.45 μm and dried under nitrogen flow. Samples were resuspended in acetonitrile
215 (10 μl) and 2 μl were used for GC-MS analysis.

216

217 2.4 Emission factor calculation

218 The UFP mass and species EFs are calculated as follows:

219

$$220 EF = C \cdot V_{spec} \quad (\text{Eq. 1})$$

221 where *EF* is the emission factor (e.g., mg/kg_{fuel}), *C* is the measured species concentration
222 (e.g., mg/m³), *V_{spec}* is the average specific flue gas volume (i.e., dry flue gas volume produced
223 per kg_{fuel}, m³/kg_{fuel}). The concentration *C* is calculated as in Eq. 2.

$$224 C = DR \cdot m / V_{sample} \quad (\text{Eq. 2})$$

225 where *DR* is the dilution ratio, *m* is the measured UFP species mass (e.g., mg), *V_{sample}* is the
226 volume extracted during the sampling period (m³).

227 The dry flue gas volume produced per kg of fuel is calculated with Eq. 3 assuming a
228 complete combustion based on the formula by Van Loo and Koppejan (2008) and averaged
229 over the sampling period:

$$230 V_{spec} = X_C \cdot V_{mol} / (M_C \cdot CO_2) \quad (\text{Eq. 3})$$

231 where, *X_C* is the fuel carbon content (kgC/kg_{fuel}), *V_{mol}* is gas molar volume (22.4 l at NTP),
232 *M_C* is carbon molar weight (12 g/mol), *CO₂* is flue gas CO₂ concentration (%_{v,dry gas}).

233

234

235 3 RESULTS AND DISCUSSION

236

237 3.1 Average flue gas conditions

238 The flue gas characteristics during the test runs are reported in Table 1 with mean values
239 and the standard deviations. The values averaged over the whole cycle may mask the lack of
240 oxygen or too high/low temperature conditions in specific combustion phases. For this reason,
241 a further parameter reflecting the combustion conditions inside the firebox is described
242 qualitatively by means of proxy variables. A combustion intensity indicator (CII) is defined
243 as the ratio of the flue gas chimney temperature (proxy for combustion temperature) and the
244 excess air ratio (EAR, i.e., ratio of the actual oxygen supply to the stoichiometric oxygen
245 need). For the comparable operating conditions, higher values of CII indicate intense
246 combustion with high burning temperatures and substantial oxygen consumption. The lower
247 values, on the other hand, represent the opposite condition in which there are low burning
248 temperatures and the air supply goes beyond the actual needs of the oxidation process in act.
249 CII is shown in Table 1 with the average value and 10th and 90th percentiles to represent the
250 critical situations.

251 While pellets combustion with the continuous operation is able to support intense
 252 combustion conditions without causing high incomplete combustion byproducts (ICB) thanks
 253 to the automatic air and fuel supply, the high CII in the wood stove, occurring during fir
 254 firewood burning brings to local situations with critical oxygen availability inducing increased
 255 ICB emissions. The combustion conditions influence both mass and composition of UFP.

256
 257 Table 1: Average (standard deviations in parentheses) flue gas conditions (@13% O₂, dry,
 258 0°C)
 259

Pellet stove (continuous)	fir	beech
Flue gas temperature (°C)	237 (1)	NA
O ₂ (% _v)	10.1 (1.1)	NA
Combustion intensity indicator	126 (109-143)*	NA
CO (mg/m ³)	142 (102)	NA
NOx (mg/m ³)	103 (9)	NA
Pellet stove (modulated)	fir	beech
Flue gas temperature (°C)	196 (38)	191 (35)
O ₂ (% _v)	13.8 (2.7)	14.0 (2.4)
Combustion intensity indicator	72 (29-123)*	69 (27-110)*
CO (mg/m ³)	273 (444)	1046 (1258)
NOx (mg/m ³)	112 (16)	232 (41)
Wood stove	fir	beech
Flue gas temperature (°C)	350 (85)	299 (83)
O ₂ (% _v)	10.8 (5.0)	14.5 (3.6)
Combustion intensity indicator	191 (42-380)*	110 (20-234)*
CO (mg/m ³)	3127 (2458)	5507 (3571)
NOx (mg/m ³)	71 (46)	114 (77)

260 * (10th percentile – 90th percentile)
 261

262 3.2 UFP concentrations, emission factors and particle number size distribution

263 Average UFP mass and number concentrations observed during the combustion
 264 experiments are referred to 13%O₂, dry conditions and 0°C and corrected for dilution. The
 265 emission factors (EFs) for fuel consumption are calculated for UFP mass and chemical
 266 constituents. Detailed data is provided in the supplementary material (Table SM3).

267 The pellet stove UFP mass concentrations average 29 mg/m³ (standard deviation: 4 mg/m³;
 268 EF: 362 mg/kg_{fuel}) for beech pellets and 34 mg/m³ (standard deviation: 18 mg/m³; EF: 434
 269 mg/kg_{fuel}) for fir pellets. No notable difference is visible in function of the wood type (fir vs.
 270 beech) and stove operation (continuous vs. modulated); even if slightly higher average values
 271 are observable for fir pellets combustion due to three samples with high UFP (namely, PF1:
 272 constant heat output - fir pellets, PF2: modulated heat output operation – fir pellets, PF3:
 273 modulated heat output operation – fir pellets). The corresponding average UFP number
 274 concentrations are 1.1·10⁸ particles/cm³ (geometric mean diameter: 38 nm) for beech pellets
 275 and 1.1·10⁸ particles/cm³ (geometric mean diameter: 75 nm) for fir pellets. The average
 276 particle number concentration is comparable for beech and fir pellets; however, the number
 277 size distribution (Figure 2) is shifted towards larger particles (remaining in the UFP size range
 278 in any case) in the latter.

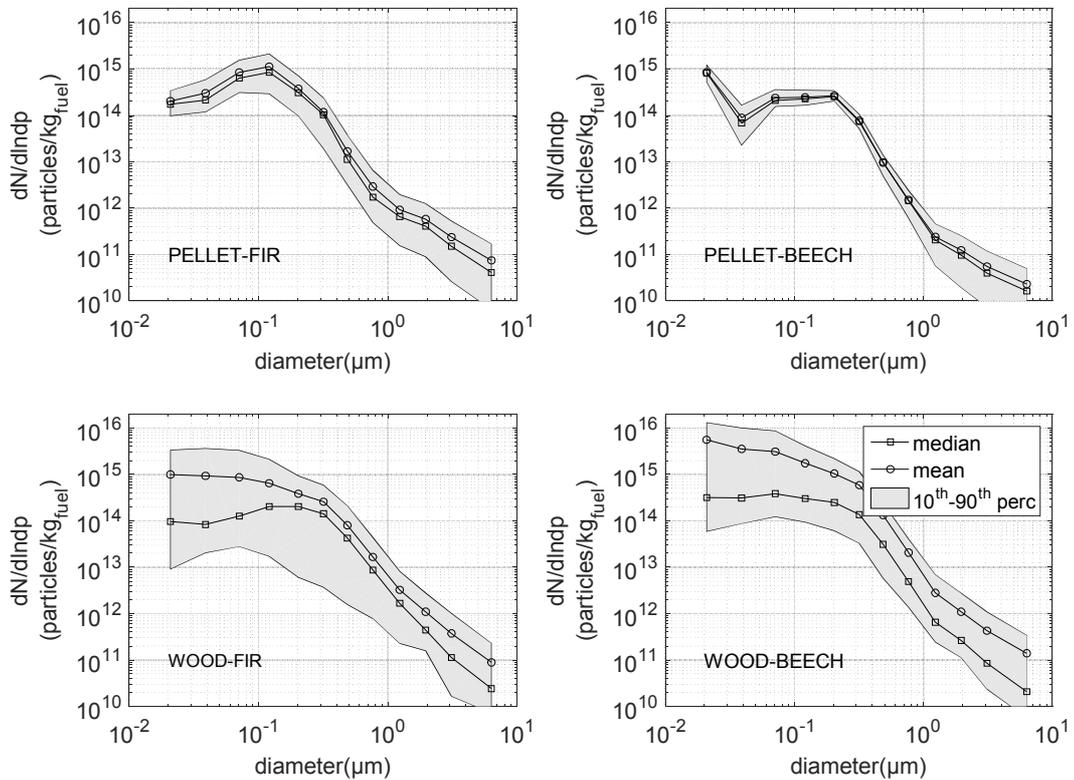
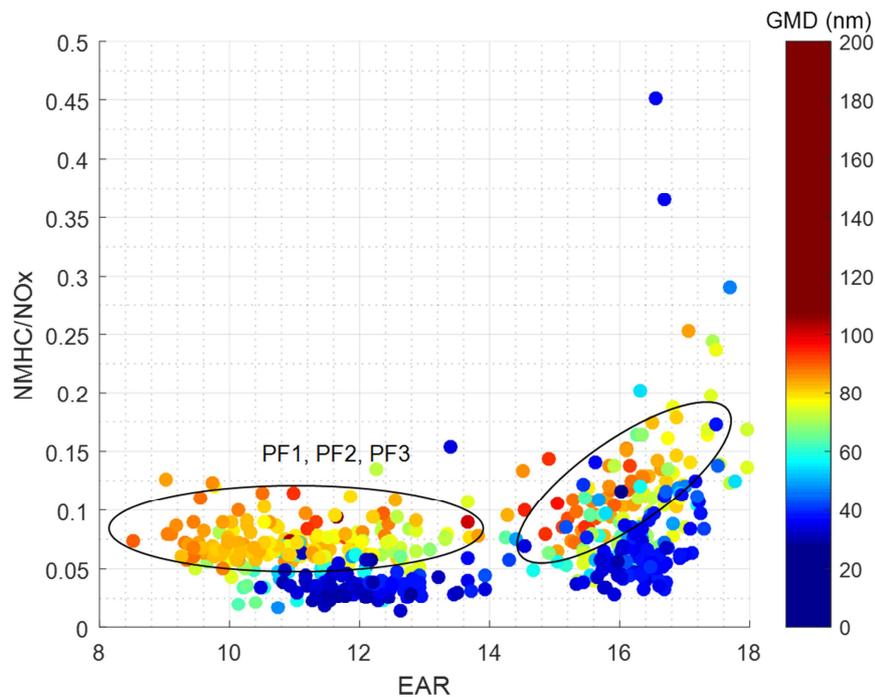


Figure 2: Particle number size distribution (particles/kg_{fuel})

279
 280
 281
 282
 283
 284
 285
 286
 287
 288
 289
 290
 291
 292
 293
 294

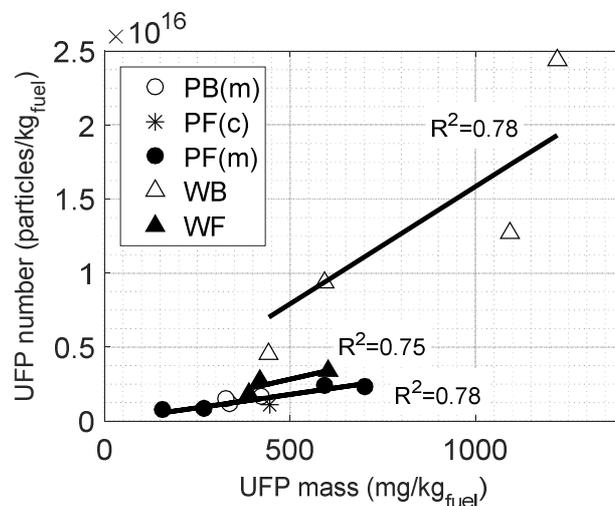
The evaluation of average flue gas and operation conditions does not bring complete clarity to the observed UFP levels in the pellet stove emissions. In order to shed light on the particular levels observed in the three abovementioned fir samples, pellet stove tests are further investigated by means of characteristic emission indicators constructed based on incomplete combustion (i.e., non methane hydrocarbons) and complete oxidation (i.e., NO_x) by-products. In order to smooth the effects directly related with the fuel composition (i.e., higher levels of pollutants for beech pellets), the NMHC emission factors are normalized by NO_x emission factors providing increased readability of the results for discriminating the single test runs. The higher values of this ratio (NMHC/NO_x) would indicate relatively less oxidative conditions inside the chamber that are expected to increase emissions of the incomplete combustion by-products. Figure 3 shows how at the parity of EAR (i.e., similar operating conditions), PF1, PF2 and PF3 are mostly characterized by higher NMHC/NO_x ratios and correspond to larger particles.



295
 296 Figure 3. NMHC/NOx ratio corresponding to different EAR. (The color scale represent the
 297 geometric mean diameter (GMD) in nm)
 298

299 The UFP mass concentrations for the wood stove average 80 mg/m^3 (standard deviation: 28
 300 mg/m^3 ; EF: $838 \text{ mg/kg}_{\text{fuel}}$) for beech firewood and 40 mg/m^3 (standard deviation: 10 mg/m^3 ;
 301 EF: $471 \text{ mg/kg}_{\text{fuel}}$) fir firewood. More variability is registered for the high ash content fuel
 302 (i.e., beech): several operational parameters such as high excess air, low burning temperatures,
 303 difficult start-up etc. bring to higher UFP emissions. The average UFP number concentrations
 304 are $7.0 \cdot 10^8 \text{ particles/cm}^3$ (geometric mean diameter: 50 nm) for beech pellets and $1.9 \cdot 10^8$
 305 particles/cm^3 (geometric mean diameter: 99 nm) for fir firewood. The particle number size
 306 distribution is shown in Figure 2. A higher variability is observed with respect to pellet
 307 experiments.

308 The linear trend lines in Figure 4, suggest a relatively constant density for pellet
 309 combustion for all operation conditions and fuel types. The situation is different for wood log
 310 combustion, where the data suggest that the density of the emitted particles vary with fuel
 311 type and variable combustion conditions.
 312



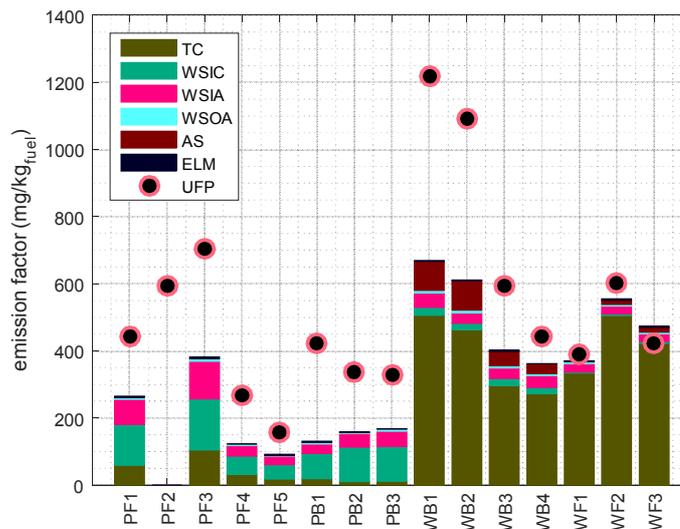
313
 314 Figure 4: UFP number vs. mass emission factors. (PF: pellet stove – fir pellets PB: pellet
 315 stove – beech pellets; (m): power modulation; (c) constant heat output; WF: wood stove – fir
 316

317 firewood; WB: wood stove – beech firewood)

318

319 3.3 Effects of stove operation and wood type on UFP composition

320 Seven classes of chemical species were analyzed in the UFP samples, namely, total carbon
321 (TC), water soluble inorganic cations (WSIC), water soluble inorganic anions (WSIA), water
322 soluble organic anions (WSOA), anhydrosugars (AS), elements (ELM), and polycyclic aromatic
323 hydrocarbons (PAH). Some species resulted to be close to or under the detection limit of the
324 related analytical technique used and were replaced by half the corresponding detection limit
325 (Table SM4 in the supplementary material). No composition results are available for PF2. The
326 composition results are discussed in terms of emission factors that can be easily converted
327 into total emissions knowing the user wood consumption (Figure 5).



328

329

330 Figure 5: UFP species emission factors ($\text{mg}/\text{kg}_{\text{fuel}}$). (PF: pellet stove – fir pellets PB: pellet
331 stove – beech pellets; WF: wood stove – fir firewood; WB: wood stove – beech firewood)

332

333 UFP emissions in the pellet stove are mostly ash-related material whereas carbonaceous
334 fraction dominates the wood stove samples reflecting the main difference between the two
335 room heaters investigated. This difference lies in the fuel feed mechanism. Automatic stoking
336 in the pellets stove enables quite constant fuel and air supply in contrast to the batch wise
337 operation of the wood stove leading to less efficient combustion due to intermittent process
338 more under influence of user dependent operational variables leading to non-optimal mixing
339 of air and fuel (Van Loo and Koppejan, 2008).

340 As expected, wood stove average TC ($400 \text{ mg}/\text{kg}_{\text{fuel}}$, range $272\text{-}506 \text{ mg}/\text{kg}_{\text{fuel}}$) is an order
341 of magnitude higher than the pellet stove ($36 \text{ mg}/\text{kg}_{\text{fuel}}$, range $10\text{-}104 \text{ mg}/\text{kg}_{\text{fuel}}$), given the
342 enhancement of the incomplete combustion conditions due to batch working process. In
343 contrast to the apparent independence of TC from the wood type fed into the wood stove, the
344 fir pellets seem to emit more TC with respect to beech pellets. The higher average TC
345 emission factor for fir pellets is caused by samples PF1 and PF3 with relatively higher TC. A
346 possible cause for higher TC content of these samples may be a decreased mixing of air and
347 fuel due to gathering heaps of ash and unburnt pellet on the hopper characteristic of these two
348 test runs. Two different situations are responsible for the emission of TC in wood log
349 combustion: lack of available oxygen in the high temperature zones in the chamber and low
350 temperature combustion with excessive oxygen. Figure 6 shows that both situations are
351 present during different batches, especially for WB1 and WB2 with difficult start-up and WF2
352 and WF3 with high temperature-low oxygen burning conditions.

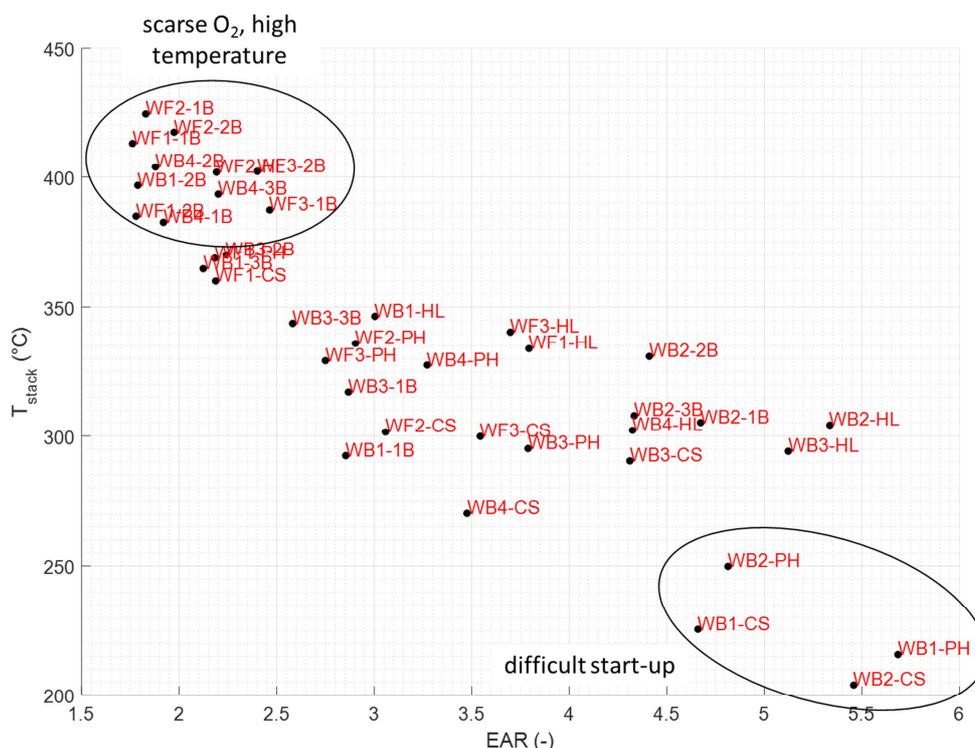


Figure 6. Per-batch average excess air ratio (EAR) vs. stack gas temperature for different test runs (PF: pellet stove – fir pellets; PB: pellet stove – beech pellets; WF: wood stove – fir firewood; WB: wood stove – beech firewood; CS: cold start; PH: pre-heating; 1B, 2B, 3B: first, second and third batches; HL: high load, final batch with burn-out period)

The average EFs for water soluble inorganic species (both cations and anions), indicative of a well-designed and operated automatic wood combustion (Nussbaumer, 2008), are three times larger in the pellet stove ($145 \text{ mg/kg}_{\text{fuel}}$, range 68-265 $\text{mg/kg}_{\text{fuel}}$) than the wood stove ($44 \text{ mg/kg}_{\text{fuel}}$, range 28-67 $\text{mg/kg}_{\text{fuel}}$). Comparable average values are obtained for fir and beech pellets for these species. The feeding of the same wood types (with slightly different composition) as wood log, besides lowering the EFs given the reasons related to the less efficient combustion mentioned above, give rise to higher inorganic emissions for the higher ash content fuel (i.e., beech wood). The disparity between pellets and wood stove water-soluble ionic species content is progressively decreasing for WSIC, WSIA and finally for WSOA. WSOA EFs are much smaller than the inorganic species. Relatively higher WSOA EFs are observed for beech wood combustion in the wood stove than the other cases investigated.

While potassium is the predominant ion in the WSIC, sulfate is the key component in the WSIA fraction of pellet UFP, without a definite trend between the two types of pellets. The importance of other minor inorganic and organic ionic species (e.g., chloride, nitrite, nitrate, calcium, acetate, formate) varies from sample to sample, again without a distinct trend depending on the pellet type, suggesting that the presence of single ionic species is more dependent on local combustion conditions than the pellet type. In fact, water soluble ionic species EFs of the two-abovementioned fir samples (PF1 and PF3) differ from the rest of the fir pellet samples. The difference, lower for PF1 (constant heat output), is mainly due to K^+ and sulfate which both show an average increase of about 3 times. This increase in correlation with the increased TC may suggest an enhanced condensation of K_2SO_4 on the carbonaceous core. Nitrite, though with much smaller EFs, shows a higher increase (about 15 times). The increase in the nitrites is also congruent with the previous observation of poor air-fuel mixing conditions in correspondence of these two samples (less nitrite is further oxidized to nitrates). Slightly higher nitrate and acetate, and a little lower Ca^{2+} is also observed for these samples.

385 Regarding the wood samples, ammonium and oxalate which are mostly absent in the pellet
386 samples are present with varying EFs in the wood samples. Ammonium EFs for the difficult
387 start-up test runs (WB1 and WB2) are twice the rest. Sulfate EFs are close to those of the
388 average pellet samples (excluding PF1 and PF3). Higher EF of K^+ is observed for the beech
389 tests without any apparent distinction between the four beech samples, whereas very low K^+
390 characterizes the fir tests. Some samples show also small quantities for Ca^{2+} and Na^{2+} .

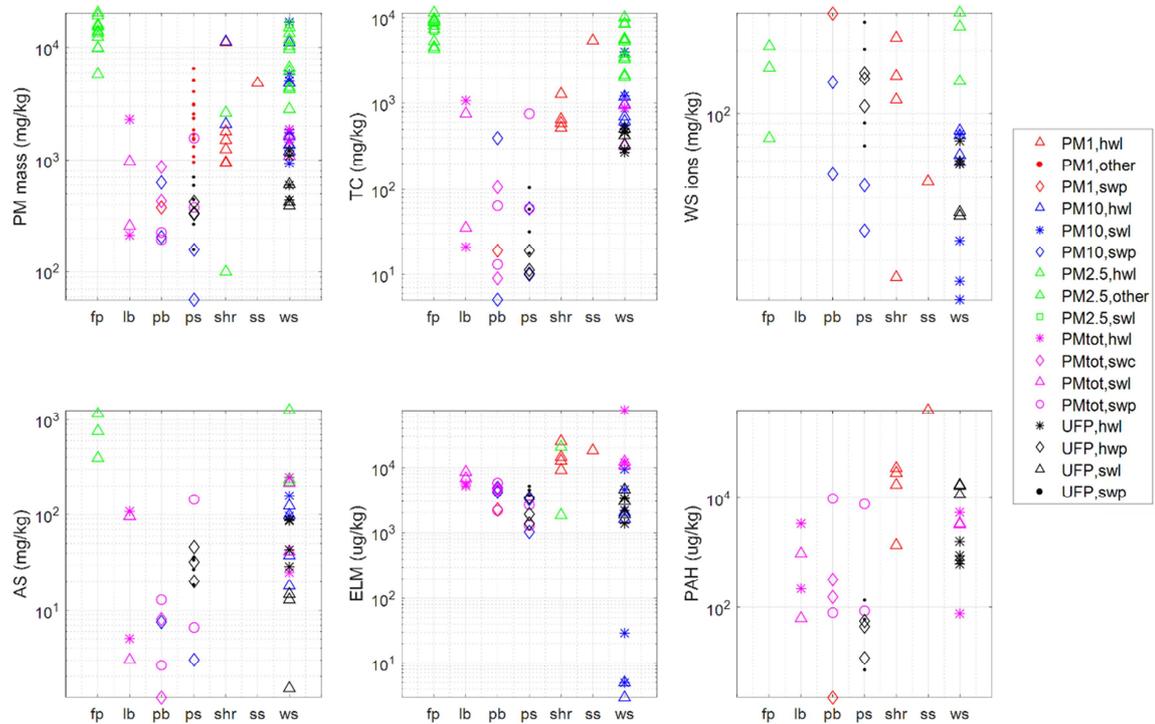
391 Anhydrosugars (i.e., levoglucosan, mannosan and galactosan) are the major organic
392 components of smoke particles from biomass burning from the breakdown of cellulose, a
393 main component of biomass, (Simoneit et al., 1999). AS are found in detectable quantities (39
394 mg/kg_{fuel} , range 2-88 mg/kg_{fuel}) only for wood stove UFP samples with beech combustion
395 leading to six-times-higher average EFs with respect to fir firewood combustion.
396 Levoglucosan is the most abundant anhydrosugar, followed by mannosan and then galactosan.
397 The lack of a discernable quantity in the pellets samples may be explained with the fact that
398 the degradation process responsible for levoglucosan formation occurs at low temperatures
399 (Kuo et al., 2008) not observed under normal operation of automatic appliances. The ratio of
400 the single species as a diagnostic tool are discussed later in section 3.4. WB1 and WB2 (i.e.,
401 difficult startup tests) show the highest AS emission factors. The lowest on the other hand
402 corresponds to a test (WF1) where rather intense combustion conditions (low excess air and
403 high temperatures) occurred (Figure 6).

404 Most of the elements detected in the UFP are those usually reported as wood constituents
405 present in variable quantities in both bark and stem. The amount of elemental species in the
406 UFP samples of both room heaters are alike (3 mg/kg_{fuel} , range 1-5 mg/kg_{fuel}). The highest
407 EFs are tendentially observed for fir pellets combustion. The divergence in function of wood
408 type (beech or fir) between the contributions of the single elements is larger in pellets
409 combustion than firewood combustion. The contribution of the various elements to the total
410 elemental content is greatly variable from sample to sample, which is probably because there
411 may be a substantial variation in metal content across the bags, even if of the same brand.
412 Zinc is the principal element followed by aluminum and iron. Other elements contributing to
413 the UFP, which are in measurable quantities, are manganese, phosphorus, chromium, copper,
414 lead, nickel and barium. Cobalt, vanadium, strontium, arsenic, cadmium, and titanium are in
415 trace quantities. Molybdenum is also in trace quantities except for beech pellet burning.
416 Manganese and lead are tendentially higher for pellet combustion. Phosphorus, chromium,
417 arsenic, cadmium, and strontium are tendentially higher for wood combustion. Nickel,
418 barium, copper, cobalt, vanadium, and titanium EFs are similar.

419 The emission factors of 8 PAHs (Phe, Ant, Flu, Pyr, BaA, Cry, BbF, BaP) are collectively
420 referred to as Σ 8PAHs. The automatically controlled and fed pellet stove has very small PAH
421 emissions (average 52 $\mu g/kg_{fuel}$, standard deviation: 46 $\mu g/kg_{fuel}$). PF1, PF3 and PB1,
422 corresponding to those with the highest pellet UFP mass, have relatively higher amounts of
423 PAH detected. EFs for wood stove are orders of magnitude larger, amounting to an average of
424 15 mg/kg_{fuel} (range 11-18 mg/kg_{fuel}) for fir wood and to 1 mg/kg_{fuel} (range 1-2 mg/kg_{fuel}) for
425 beech wood burning. The lowest excess oxygen and the highest temperatures reached during
426 fir firewood experiments hinted to very intense combustion conditions favoring the formation
427 of PAH species. PAH fingerprints are provided in the supplementary material (Figure FSM1).
428 The proportion of lower MW PAHs (i.e., 3- and 4- ring isomers, Phe, Ant, Flu, Pyr) in the
429 Σ 8PAHs is higher for the pellets samples, whereas wood samples are enriched in higher MW
430 PAHs (i.e., 4- and 5- ring isomers, BaP, BbF, Cry, BaA). The PAHs measured by the study
431 and defined by the International Agency for Research on Cancer (IARC, 2016) as group 1-
432 carcinogenic (i.e., BaP) and group 2B-possibly carcinogenic to humans (i.e., BaA, Cry, BbF)
433 account on average for the 85% of Σ 8PAHs for the wood stove samples. The corresponding
434 value for the two pellets samples with the highest EFs is much lower (average ~19%).

435 Figure 7 shows a comparison between the present study and the literature values for
436 different types of residential heating appliances fed with different type of fuels (details and
437 references in Table SM5 in the supplementary material). The reported emission factors are

438 extremely variable. To reduce the effect of high and low extremes in the data only median
 439 values are compared. Even though the EFs are obtained with different sampling
 440 methodologies and for different size fractions, for mass and elements generally similar
 441 emission factors are observed for automatic pellet appliance in our study. While about three
 442 times lower TC and 60 times lower PAHs, and 3 - 5 times higher water soluble ions and
 443 anhydrosugars are found. For manually fed appliances on the other hand, 2 - 8 times lower
 444 emission factors are obtained for both mass and composition in comparison with the literature.
 445



446
 447 Figure 7. Comparison of literature PM mass emission factors and composition with the
 448 present study (fuel types – hwl: hardwood logs; swl: softwood logs; hwp: hardwood pellets;
 449 swp: softwood pellets; swc: softwood chips; other: various biomass) (appliance types – fp:
 450 fireplace; lb: logwood boiler; pb: pellet/chip boiler; ps: pellet stove; shr: slow heat release
 451 appliance; ss: sauna stove; ws: wood stove), (PM fractions – black: UFP; red: PM1; green:
 452 PM2.5; blue: PM10; magenta: PMtot) (details and references in Table SM5 in the
 453 supplementary material)
 454

455 3.4 Diagnostic ratios

456 PAH diagnostic ratios:

457 The binary ratio method for PAH source identification involves comparing ratios of pairs
 458 of frequently found PAH species (Ravindra et al., 2008). Generally the ratios of the principal
 459 parent PAHs with MW 178 [Phe and Ant], 202 [Flu and Pyr], and 228 [BaA and Cry] are
 460 used as diagnostic tracers for source characterization of biomass burning emissions as
 461 compared with fossil-fuel combustion (Rajput et al., 2014, Ding et al., 2007).

462 Given the very low emission factors from pellet combustion, the present discussion involves
 463 only wood stove emissions. PAH content of the UFP samples reflect the conditions in the
 464 approximate vicinity of the emission source: the sample is diluted and cooled triggering the gas-
 465 to-particulate conversion but it excludes the degradation of PAH species due to atmospheric
 466 ageing.

467 Even if not directly comparable due to different sampling methodologies, size fractions,
 468 combustion appliances and dilution conditions considered, the experimental diagnostic ratios
 469 are presented in comparison with several others found in literature (Table SM6 in the
 470 supplementary material). BbF/Flu is one of the ratios proposed as a signature factor to identify

471 the sources of particulate PAHs in the atmosphere (Fu et al., 2010). The PM10 emission
472 samples in the cited study have shown much higher BbF/Flu ratios (~3.7) for woody biomass
473 burning aerosol than aerosols originating from the burning of diesel fuel and gasoline (0.047-
474 0.050). The BbF/Flu ratio in the present study on UFP fraction ranges between 3.6-11.0
475 (average 6.9). Other binary diagnostic ratios reported in the literature for vehicle exhaust are ~1
476 and ~10 (Pyr/BaP ratios), and 0.73 and 0.5 (BaP/[BaP+Cry] ratios), respectively from gasoline
477 and diesel vehicles, and 0.6 for Flu/Pyr ratio from generic vehicular emissions species
478 (Ravindra et al., 2008). The corresponding average values (ranges reported in parentheses) for
479 this study are 0.33 (0.25-0.55), 0.59 (0.33-.89), and 0.80 (0.43-1.00) respectively for Pyr/BaP,
480 BaP/[BaP+Cry], and Flu/Pyr. Guillon et al. (2013) report Phe/(Phe+Ant), Flu/(Flu+Pyr) and
481 BaA/BaP ratios in the PM2.5 samples of several biomass species with averages respectively of
482 0.84, 0.49 and 1.46. Corresponding experimental findings in the present study are respectively
483 0.78 (0.61-0.88), 0.44 (0.30-0.50), and 0.61 (0.41-0.81).

484 The comparison of the ratios reported in literature with the experimental results shows that
485 BaP/[BaP+Cry] is not a good diagnostic ratio to differentiate vehicular emissions and wood
486 combustion. On the other hand, BbF/Flu, Pyr/BaP, and Flu/Pyr resulted to be potentially good
487 wood burning tracers. However, one has to keep in mind that the variation of environmental
488 conditions (photochemistry, oxidative processes, mixing of air masses etc.) may influence some
489 of these ratios (Guillon et al., 2013), thus the applicability as a marker for source evaluation
490 should be assessed case by case. For example, BaP is reported to degrade much faster than its
491 isomer in the atmosphere so the ratios in fresh and aged emissions will be different. Other
492 isomer pairs such as for instance Flu/Pyr, on the other hand, photolytically degrade at
493 comparable rates, preserving thus the original compositional information during atmospheric
494 transport (Ding et al., 2007).

495 Figure 8 shows the diagnostic ratios calculated on the UFP emission samples of this study
496 and ambient UFP sample averages from an Alpine village dominated by biomass combustion
497 (both pellets and wood log) in the winter months (TOBICUP project ambient sampling results
498 reported elsewhere, Dell'Acqua et al., 2016). BbF/(BbF+BaP) and Phe/(Phe+Ant) ratios in the
499 ambient samples are relatively close (\pm ~20%) to emission ratios. Other ambient ratios are
500 mostly lower than the emission ratios (except for Pyr/BaP ratio which is higher), suggesting
501 both the effects of an additional emission source and the alteration in the ratios by the
502 abovementioned atmospheric processes.

503

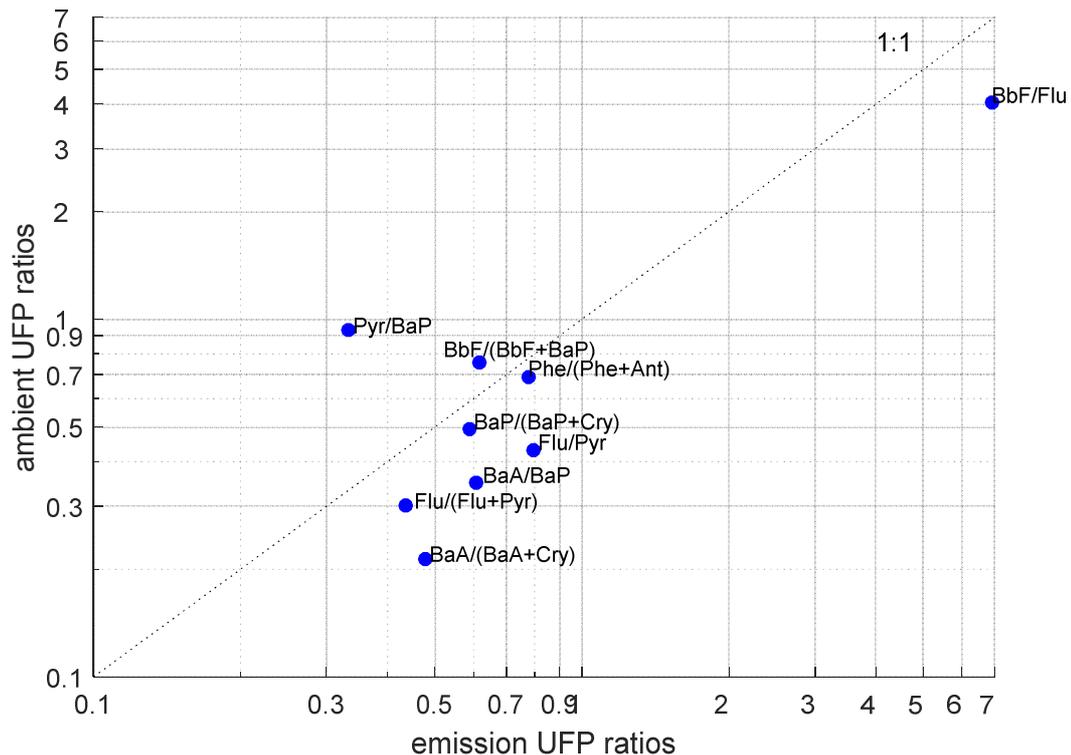


Figure 8: PAH median diagnostic ratios for emission and ambient UFP samples

Anhydrosugar diagnostic ratios

Other characteristic ratios that can be compiled from experimental data in the present study are the levoglucosan-to-mannosan (lev/man) and the levoglucosan-to-galactosan (lev/gal) ratios. The former ratio can provide insights into the specific types of biomass (the hardwood and softwood types) burned (AIRUSE, 2013). The experimental ratios calculated from the emission factors are on average 4 (range 3-5) for the fir wood (softwood) and 15 (range 12-18) for the beech wood (hardwood). The lev/gal ratio on the other hand is proposed to discriminate between organic combustion emissions from foliar material and from wood log combustion (Schimdl et al., 2008). The ratios calculated in the present study are on average 43 (range 15-87) for the fir wood and slightly lower for beech wood averaged at 28 (range 27-32). Both characteristic ratios obtained in the present study for UFP size fraction are consistent with the values reported in literature for larger particle size fractions (Schimdl et al., 2008 and the references therein).

4 CONCLUSIONS

The UFP levels are observed to be fairly variable between the test runs. While differences found among the UFP levels of the wood stove samples are explained in relation to the main stove operational parameters inherent to single test runs and the firewood type used, the same evaluation does not bring complete clarity to the observed UFP levels in the pellet stove emissions. As expected, the combustion intensity in the automatic appliance is regulated more by the operation mode than the pellets type: however, note that both pellet types used in the study were made of virgin woody biomass; the same observation would probably not hold if a non-woody biomass fuel were used. On the other hand, in the wood stove the combustion characteristics are strictly connected with the firewood type.

The generally more complete combustion thanks to the automatic fuel and air supply, and better air-fuel mixing causes the release of more water soluble inorganic species and less carbonaceous material in the UFP. However local situations such as for example pellet heaps

536 on the burner pot may enhance the formation of incomplete combustion byproducts due to
537 decreased air-fuel mixing, which alter also the composition of the UFP with relatively higher
538 TC and PAH. Higher ash content of the fuel (i.e., beech) influences the number size
539 distribution, generating relatively smaller particles with respect to lower ash pellets (e.g., A1
540 certificate fir pellets) which remain mostly in the UFP range in any case.

541 The present study confirmed that manually fed room heaters are susceptible to involuntary
542 malpractice (e.g., difficult startup due to inadequate air control valve regulations) even if they
543 are conducted following the manufacturer instructions. Critical situations in terms of lack of
544 available oxygen for the complete oxidation and high temperatures occur during fir firewood
545 combustion in the wood stove. This situation enhances especially the PAH emission factors.
546 Another crucial aspect consists of the non-optimal combustion conditions caused by overall
547 low burning temperatures and air supply much above the stoichiometric need, observed
548 especially in the wood stove experiments burning high ash fuel with difficult startup period.
549 These experiments correspond to particularly high UFP EFs with relatively smaller particle
550 sizes together with increased TC and anhydrosugars release.

551 Interestingly, UFP elemental species release is apparently independent of the stove and
552 wood type used.

553 In summary, the results of the study demonstrate that the burning of the same wood types
554 as logs in a manual appliance instead of as pellet (much drier and smaller) in an automatic
555 roomheater may cause not only the increase of UFP emissions (especially in case of high ash
556 content fuels) but also the alteration of the composition with potentially more carcinogenic
557 substances (PAH fingerprint shifts towards more carcinogenic higher MW PAHs).

558

559 **5 REFERENCES**

560

561 AIRUSE, LIFE11 ENV/ES/584. Milestone Identification of biomass burning tracers. Action
562 B4. Coordinated by: Universidade de Aveiro. (Last access: June 2016: [http:// airuse.eu/wp-](http://airuse.eu/wp-content/uploads/2013/11/B4-MILESTONE-tracers-biomass.pdf)
563 [content/uploads/2013/11/B4-MILESTONE-tracers-biomass.pdf](http://airuse.eu/wp-content/uploads/2013/11/B4-MILESTONE-tracers-biomass.pdf))

564 Bernardoni V., Cuccia E., Calzolari G., Chiari M., Lucarelli F., Massabò D., Nava S., Prati P.,
565 Valli G., Vecchi R., 2011. ED-XRF set-up for size-segregated aerosol samples analysis. *X-*
566 *Ray Spectrometry* 40, 79–87. doi: 10.1002/xrs.1299.

567 Boman C., Nordin A., Bostrom D., Ohman M., 2004. Characterization of inorganic particulate
568 matter from residential combustion of pelletized biomass fuels. *Energy and Fuels* 18, 338-348.

569 Cassee F.R., Héroux M.E., Gerlofs-Nijland M.E., Kelly F.J., 2013. Particulate matter beyond
570 mass: recent health evidence on the role of fractions, chemical constituents and sources of
571 emission. *Inhalation Toxicology* 25(14), 802–812. doi:10.3109/08958378.2013.850127.

572 Denier van der Gon H.A.C., Bergström R., Fountoukis C., Johansson C., Pandis S.N.,
573 Simpson D., Visschedijk A.J.H., 2015. Particulate emissions from residential wood
574 combustion in Europe – revised estimates and an evaluation. *Atmospheric Chemistry and*
575 *Physics* 15, 6503–6519. doi:10.5194/acp-15-6503-2015.

576 Díaz-Robles L.A., Fub J.S., Vergara-Fernández A., Etcharren P., Schiappacasse L.N., Reed
577 G.D., Silva M.P., 2014. Health risks caused by short term exposure to ultrafine particles
578 generated by residential wood combustion: A case study of Temuco, Chile. *Environment*
579 *International* 66, 174–181. doi:10.1016/j.envint.2014.01.017.

580 Ding X., Wang X.M., Xi Z.Q., Xiang C.H., Mai B.X., Sun L.G., Zheng M., Sheng G.Y., Fu
581 J.M., Pöschl U., 2007. Atmospheric polycyclic aromatic hydrocarbons observed over the
582 North Pacific Ocean and the Arctic area: Spatial distribution and source identification.
583 *Atmospheric Environment* 41, 2061–2072. doi:10.1016/j.atmosenv.2006.11.002.

584 Fernandes U., Costa M., 2012. Particle emissions from a domestic pellets-fired boiler. *Fuel*

- 585 Processing Technology 103, 51–56. doi:10.1016/j.fuproc.2011.08.020.
- 586 Fu F., Tian B., Lin G., Chen Y., Zhang J., 2010. Chemical characterization and source
587 identification of polycyclic aromatic hydrocarbons in aerosols originating from different
588 sources. *Journal of the Air & Waste Management Association* 60(11), 1309-1314.
- 589 Guillon A., Le Ménach K., Flaud P.M., Marchand N., Budzinski H., Villenave E., 2013.
590 Chemical characterization and stable carbon isotopic composition of particulate Polycyclic
591 Aromatic Hydrocarbons issued from combustion of 10 Mediterranean woods. *Atmospheric*
592 *Chemistry Physics* 13, 2703–2719. doi:10.5194/acp-13-2703-2013.
- 593 IARC, 2016. IARC monographs on the evaluation of carcinogenic risk to humans. List of
594 classifications, volumes 1–116. <http://monographs.iarc.fr/ENG/Classification/index.php>.
595 (Last consulted July 2016)
- 596 Lamberg H., Nuutinen K., Tissari J., Ruusunen J., Yli-Pirilä P., Sippula O., Tapanainen M.,
597 Jalava P., Makkonen U., Teinilä K., Saarnio K., Hillamo R., Hirvonen M.R., Jokiniemi J.,
598 2011. Physicochemical characterization of fine particles from small-scale wood combustion.
599 *Atmospheric Environment* 45, 7635–7643. doi:10.1016/j.atmosenv.2011.02.072.
- 600 Leskinen J., Tissari J., Uski O., Virén A., Torvela T., Kaivosoja T., Lamberg H., Nuutinen I.,
601 Kettunen T., Joutsensaari J., Jalava P.I., Sippula O., Hirvonen M.R., Jokiniemi J., 2014. Fine
602 particle emissions in three different combustion conditions of a wood chip-fired appliance e
603 Particulate physico-chemical properties and induced cell death. *Atmospheric Environment* 86
604 (2014) 129-139. <http://dx.doi.org/10.1016/j.atmosenv.2013.12.012>.
- 605 Longhin E., Gualtieri M., Capasso L., Bengalli R., Mollerup S., Holme J.A., Øvrevik J.,
606 Casadei S., Di Benedetto C., Parenti P., Camatini M., 2016. Physico-chemical properties and
607 biological effects of diesel and biomass particles. *Environmental Pollution* 215, 366-375.
- 608 Nussbaumer T., 2008. Particulate Emissions from Biomass Combustion in IEA Countries
609 Survey on Measurements and Emission Factors. [http://www.ieabcc.nl/publications](http://www.ieabcc.nl/publications/Nussbaumer_et_al_IEA_Report_PM10_Jan_2008.pdf)
610 [/Nussbaumer_et_al_IEA_Report_PM10_Jan_2008.pdf](http://www.ieabcc.nl/publications/Nussbaumer_et_al_IEA_Report_PM10_Jan_2008.pdf)
- 611 Obaidullah M., Bram S., Verma V.K., De Ruyck J., 2012. A review on particle emissions
612 from small scale biomass combustion. *International Journal of Renewable Energy Research* 2
613 (1).
- 614 Ozgen S., Cernuschi S., Giugliano M., 2013. Experimental evaluation of particle number
615 emissions from wood combustion in a closed fireplace. *Biomass and Bioenergy* 50, 65–74.
616 doi:10.1016/j.biombioe.2013.01.015.
- 617 Ozgen S., Caserini S., Galante S., Giugliano M., Angelino E., Marongiu A., Hugony F.,
618 Migliavacca G., Morreale C., 2014. Emission factors from small scale appliances burning
619 wood and pellets. *Atmospheric Environment* 94, 144–153.
620 doi:10.1016/j.atmosenv.2014.05.032.
- 621 Park S.S., Sim S.Y., Bae M.S., Schauer J.J., 2013. Size distribution of water-soluble
622 components in particulate matter emitted from biomass burning. *Atmospheric Environment*
623 73, 62-72. <http://dx.doi.org/10.1016/j.atmosenv.2013.03.025>.
- 624 Perrone M.R., Becagli S., Garcia Orza J.A., Vecchi R., Dinoi A., Udisti R., Cabello M., 2013.
625 The impact of long-range-transport on PM1 and PM2.5 at a Central Mediterranean site.
626 *Atmospheric Environment* 71, 176–186. doi:10.1016/j.atmosenv.2013.02.006.
- 627 Piazzalunga A., Bernardoni V., Fermo P., Vecchi R., 2013. Optimisation of analytical
628 procedures for the quantification of ionic and carbonaceous fractions in the atmospheric
629 aerosol and applications to ambient samples. *Analytical and Bioanalytical Chemistry* 405,
630 1123–1132. doi: 10.1007/s00216-012-6433-5.
- 631 Ravindra K., Sokhia R., Van Grieken R., 2008. Atmospheric polycyclic aromatic

- 632 hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment*
633 42, 2895–2921. doi:10.1016/j.atmosenv.2007.12.010.
- 634 Rajput P., Sarin M.M., Sharma D., Singh D., 2014. Atmospheric polycyclic aromatic
635 hydrocarbons and isomer ratios as tracers of biomass burning emissions in Northern India.
636 *Environmental Science Pollution Research* 21, 5724–5729. doi: 10.1007/s11356-014-2496-5.
- 637 Saarnio K., 2013. Chemical characterisation of fine particles from biomass burning. PhD
638 dissertation. Finnish Meteorological Institute Contributions No. 97 FMI-CONT-97. Date:
639 October 2013. ISBN 978-951-697-792-1 (pdf). <http://ethesis.helsinki.fi>
- 640 Schmidl C., Bauer H., Dattler A., Hitzenberger R., Weissenboeck G., Marr I.L., Puxbaum H.,
641 2008. Chemical characterisation of particle emissions from burning leaves. *Atmospheric*
642 *Environment* 42, 9070–9079. doi:10.1016/j.atmosenv.2008.09.010.
- 643 Simoneit B.R.T., Schauer J.J., Nolte C.G., Oros D.R., Elias V.O., Fraser M.P., Rogge W.F.,
644 Cass G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric
645 particles. *Atmospheric Environment* 33, 173–182.
- 646 Sippula O., 2010. Fine particle formation and emissions in biomass combustion. Report Series
647 in Aerosol Science. No: 108. Date: March 2010. ISBN 978-952-5822-15-1 (PDF version).
648 <http://www.atm.helsinki.fi/FAAR>
- 649 Tissari J., Lyyranen J., Hytonen K., Sippula O., Tapper U., Frey A., Saarnio K., Pennanen
650 A.S., Hillamo R., Salonen R.O., Hirvonen M.-R., Jokiniemi J., 2008. Fine particle and
651 gaseous emissions from normal and smouldering wood combustion in a conventional masonry
652 heater. *Atmospheric Environment* 42, 7862-7873. doi:10.1016/j.atmosenv.2008.07.019.
- 653 Torvela T., Tissari J., Sippula O., Kaivosoja T., Leskinen J., Virén A., Lähde A., Jokiniemia
654 J., 2014. Effect of wood combustion conditions on the morphology of freshly emitted fine
655 particles. *Atmospheric Environment* 87, 65-76.
656 <http://dx.doi.org/10.1016/j.atmosenv.2014.01.028>.
- 657 Van Loo S., Koppejan J., 2008. *The Handbook of. Biomass Combustion and Co-firing.*
658 London: Earthscan.
- 659 Vicente E.D., Duarte M.A., Calvo A.I., Nunes T.F., Tarelho L.A.C., Custódio D., Colombi C.,
660 Gianelle V., Sanchez de la Campa A., Alves C.A., 2015. Influence of operating conditions on
661 chemical composition of particulate matter emissions from residential combustion.
662 *Atmospheric Research* 166, 92–100. doi:10.1016/j.atmosres.2015.06.016.
- 663 Wiinikka H., Gebart R., Boman C., Bostrom D., Nordin A., Ohman M., 2006. High-
664 temperature aerosol formation in wood pellets flames: Spatially resolved measurements.
665 *Combustion and Flame* 147, 278–293. doi:10.1016/j.combustflame.2006.08.009.

666

6 ACKNOWLEDGEMENTS

The TOBICUP project is founded by CARIPO foundation (Grant 2013-1040). The authors would also like to thank Gruppo Piazzetta, Caminetti & Stufe for the pellet and wood stoves used in the study.

References in the supplementary material TSM5

Alves C., Gonçalves C., Fernandes A.P., Tarelho L., Pio C., 2011. Fireplace and woodstove fine particle emissions from combustion of western Mediterranean wood types. *Atmospheric Research* 101, 692-700. doi:10.1016/j.atmosres.2011.04.015

Boman C., Nordin A., Bostrom D., Ohman M., 2004. Characterization of inorganic particulate matter from residential combustion of pelletized biomass fuels. *Energy and Fuels* 18, 338-348.

Calvo A.I., Martins V., Nunes T., Duarte M., Hillamo R., Teinila K., Pont V., Castro A., Fraile R., Tarelho L., Alves C., 2015. Residential wood combustion in two domestic devices: Relationship of different parameters throughout the combustion cycle. *Atmospheric Environment* 116, 72-82. doi:10.1016/j.atmosenv.2015.06.012.

Hedberg E., Kristensson A., Ohlsson M., Johansson C., Johansson P.A., Swietlicki E., Veselya V., Wideqvist U., Westerholme R., 2002. Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmospheric Environment* 36, 4823-4837.

Lamberg H., Nuutinen K., Tissari J., Ruusunen J., Yli-Pirilä P., Sippula O., Tapanainen M., Jalava P., Makkonen U., Teinilä K., Saarnio K., Hillamo R., Hirvonen M.R., Jokiniemi J., 2011. Physicochemical characterization of fine particles from small-scale wood combustion. *Atmospheric Environment* 45, 7635-7643. doi:10.1016/j.atmosenv.2011.02.072.

Orasche J., Seidel T., Hartmann H., Schnelle-Kreis J., Chow J., Ruppert H., Zimmermann R., 2012. Comparison of emissions from wood combustion. Part 1: emission factors and characteristics from different small-scale residential heating appliances considering particulate matter and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential of particle-bound organic species. *Energy Fuels* 26, 6695-6704. dx.doi.org/10.1021/ef301295k.

Schmidl C., Lüsser M., Padouvas E., Lasselsberger L., Rzáca M., Ramirez-Santa Cruz C., Handler M., Peng G., Bauer H., Puxbaum H., 2011. Particulate and gaseous emissions from manually and automatically fired small scale combustion systems. *Atmospheric Environment* 45, 7443-7454. doi:10.1016/j.atmosenv.2011.05.006.

Tissari J., Lyyranen J., Hytonen K., Sippula O., Tapper U., Frey A., Saarnio K., Pennanen A.S., Hillamo R., Salonen R.O., Hirvonen M.-R., Jokiniemi J., 2008. Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. *Atmospheric Environment* 42, 7862-7873. doi:10.1016/j.atmosenv.2008.07.019.

Vicente E.D., Duarte M.A., Calvo A.I., Nunes T.F., Tarelho L., Alves C.A., 2015. Emission of carbon monoxide, total hydrocarbons and particulate matter during wood combustion in a stove operating under distinct conditions. *Fuel Processing Technology* 131, 182-192.

Highlights:

- Ultrafine particle ($dp < 100\text{nm}$) chemical constituent emission factors are provided
- Automatic and manually fed room heaters with two wood types are investigated
- Tests conducted with appliances working under real-world operating conditions
- Increased emissions (UFP, NO_x , CO) for increased fuel ash content in the wood stove
- PAH fingerprint shifts towards more carcinogenic PAH in wood stove UFP