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

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

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

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

Our previous experience has shown the importance of capturing the emission characteristics in the proximity of the source when the flue gas exiting the chimney is not fully diluted and the particulate matter emissions have not yet completely undergone oxidation by reactive atmospheric species (Ozgen et al., 2013). Taking into account the fact that the limited emission height of domestic heating appliances may increase the exposure of the population living nearby the source, the current study is designed also to reflect, as close as possible, the changes in the emissions, enhancing the dynamic processes involving the particles, exhausting the potential of the flue gas to condense upon further cooling.

2 EXPERIMENTAL SECTION

2.1 Combustion appliances and test fuels

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

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

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

2.2 Experimental details

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

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

For the wood stove, the burning cycle (5-7 hours, detailed information in Table SM2, supplementary material) comprised the loading of four to five consecutive batches comprising the cold start, eventual preheating period, two nominal loads and a final high load batch including the burn-out period. The start up batch consisted of small wood logs, fir wood sticks and of kerosene based fire starter. The initial batch was ignited from the top. During some tests the furnace was further preheated after the cold start with additional small batches. Afterwards, two batches of nominal load (about 2 kg/h, ~20 cm x ~11 cm x ~8 cm pieces) were loaded. The burning cycle was concluded with a higher load batch (about 1.3 times the nominal load) with slightly bigger logs. The start-up and loading procedure followed the prescriptions of the manufacturer. During loading of a new batch, the air control levers (both primary and secondary air) and the stove door were kept open for a lapse of time to permit the wood to catch fire, then the door was closed and the air control levers were set to nominal position. The unburned residues and inorganic ash were removed from the appliance and the firebox cleaned at the end of each test day.

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

For the pellets stove tests the flue gas was directly extracted (point 5 in Figure 1) from the chimney of the appliance and sent to the UFP sampling system (scheme A in Figure 1) described in section 2.3. While during the wood stove experiments, the flue gas was extracted from the dilution tunnel (point 7 in Figure 1) to further enhance the gas-to-particle conversion of the semi-volatile products of combustion. The average dilution ratio monitored in the dilution tunnel through simultaneous CO_2 measurements in the chimney and the tunnel, was about 16. The chimney gas was cooled and mixed with the indoor air upstream of the extractive sampling locations (point 8 in Figure 1), before being sent to the UFP sampling system (scheme A in Figure 1) described in section 2.3, the same as the one used for the pellets stove.

The gaseous compounds (CO, CO_2, organic gaseous compounds (OGC) divided in methane and non-methane hydrocarbons (NMHC), NOx, O_2) and the flue gas temperature were also monitored throughout the testing period.

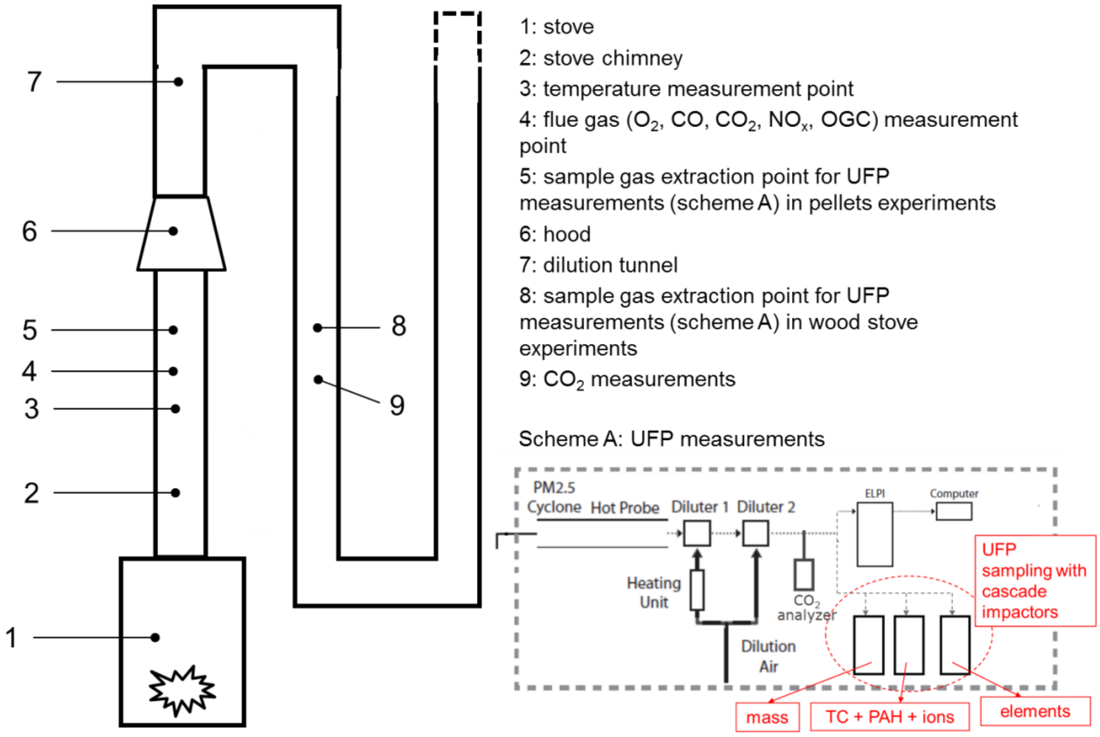

Figure 1: Experimental set up for residential solid fuel appliance testing

2.3 UFP sampling and chemical characterization

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

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

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

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

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

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

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

- elements (ELM) → Elements (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, P, Pb, Sr, Ti, V, Zn) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Varian 720-ES). Solubilization procedure followed the EN14902:2005 methodology by using concentrate sub-boiled distilled HNO_3 and 30% ultrapure H_2O_2 in a microwave oven, at 220°C for 25 min (P= 55 bar) (Perrone et al., 2013).

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

2.4 Emission factor calculation

The UFP mass and species EFs are calculated as follows:

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

where EF is the emission factor (e.g., mg/kg$_{\text{fuel}}$), C is the measured species concentration (e.g., mg/m^3), V_{spec} is the average specific flue gas volume (i.e., dry flue gas volume produced per kg$_{\text{fuel}}$, m^3/kg$_{\text{fuel}}$). The concentration C is calculated as in Eq. 2.

$$C = DR \cdot m \;\big/\; V_{sample} \qquad \text{(Eq. 2)}$$

where DR is the dilution ratio, m is the measured UFP species mass (e.g., mg), V_{sample} is the volume extracted during the sampling period (m^3).

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

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

where, X_C is the fuel carbon content (kgC/kgfuel), V_{mol} is gas molar volume (22.4 l at NTP), M_C is carbon molar weight (12 g/mol), CO_2 is flue gas CO_2 concentration (%$_{\text{v,dry gas}}$).

3 RESULTS AND DISCUSSION

3.1 Average flue gas conditions

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

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

Table 1: Average (standard deviations in parentheses) flue gas conditions (@13% O_2, dry, 0°C)

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)

* (10th percentile – 90th percentile)

3.2 UFP concentrations, emission factors and particle number size distribution

Average UFP mass and number concentrations observed during the combustion experiments are referred to 13%O_2, dry conditions and 0°C and corrected for dilution. The emission factors (EFs) for fuel consumption are calculated for UFP mass and chemical constituents. Detailed data is provided in the supplementary material (Table SM3).

The pellet stove UFP mass concentrations average 29 mg/m^3 (standard deviation: 4 mg/m^3; EF: 362 mg/kg$_{fuel}$) for beech pellets and 34 mg/m^3 (standard deviation: 18 mg/m^3; EF: 434 mg/kg$_{fuel}$) for fir pellets. No notable difference is visible in function of the wood type (fir vs. beech) and stove operation (continuous vs. modulated); even if slightly higher average values are observable for fir pellets combustion due to three samples with high UFP (namely, PF1: constant heat output - fir pellets, PF2: modulated heat output operation – fir pellets, PF3: modulated heat output operation – fir pellets). The corresponding average UFP number concentrations are $1.1 \cdot 10^8$ particles/cm^3 (geometric mean diameter: 38 nm) for beech pellets and $1.1 \cdot 10^8$ particles/cm^3 (geometric mean diameter: 75 nm) for fir pellets. The average particle number concentration is comparable for beech and fir pellets; however, the number size distribution (Figure 2) is shifted towards larger particles (remaining in the UFP size range in any case) in the latter.

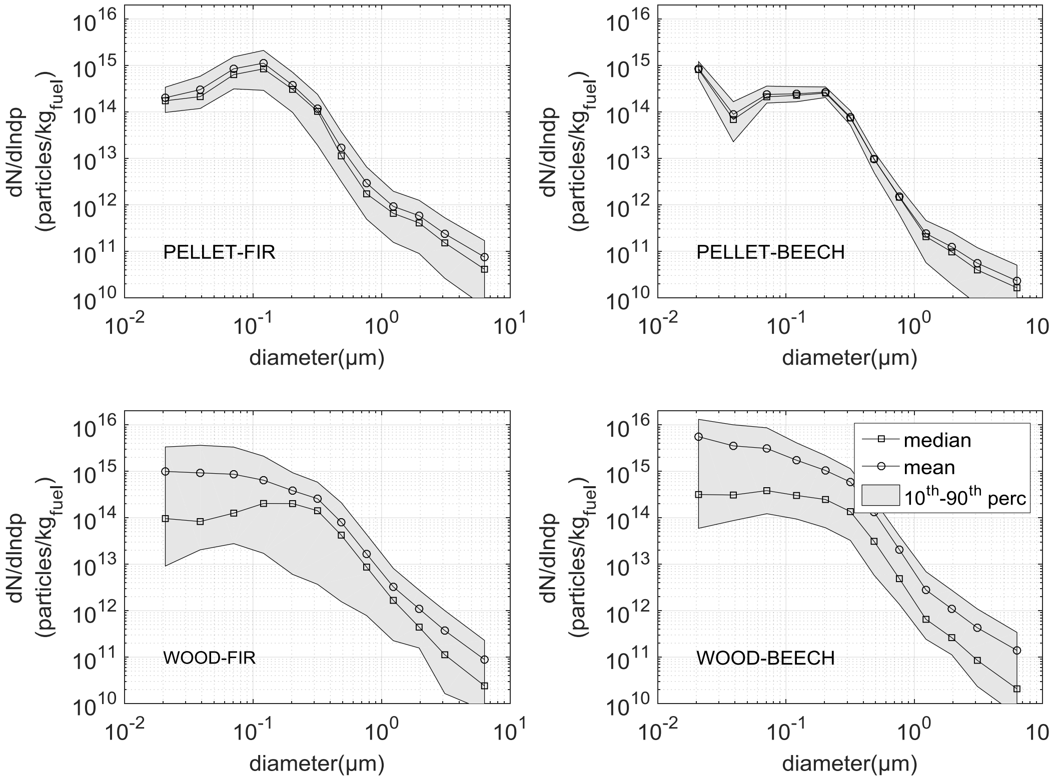

Figure 2: Particle number size distribution (particles/kg$_{fuel}$)

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., NOx) 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 NOx emission factors providing increased readability of the results for discriminating the single test runs. The higher values of this ratio (NMHC/NOx) 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/NOx ratios and correspond to larger particles.

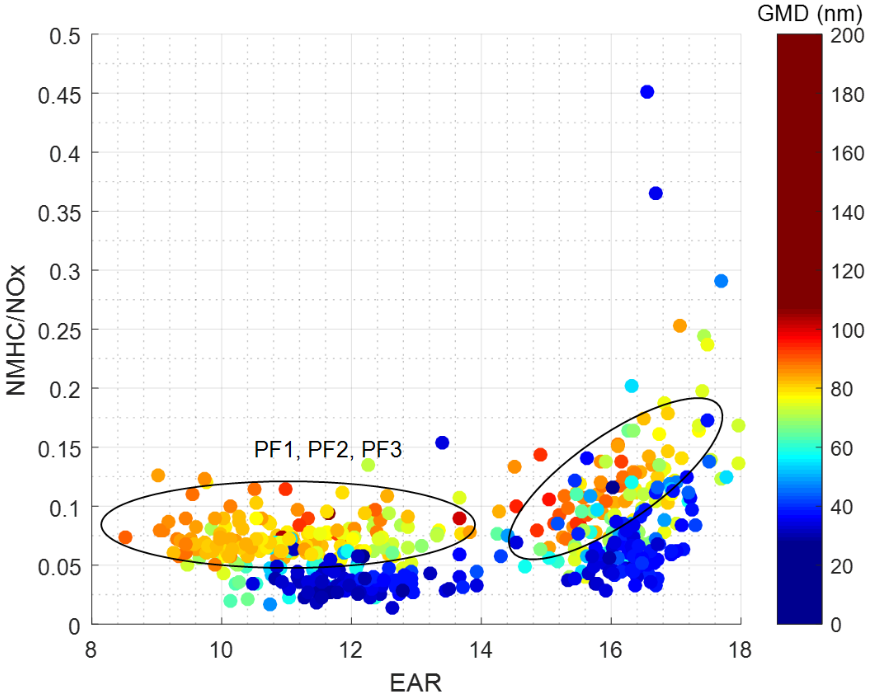

Figure 3. NMHC/NOx ratio corresponding to different EAR. (The color scale represent the geometric mean diameter (GMD) in nm)

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

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

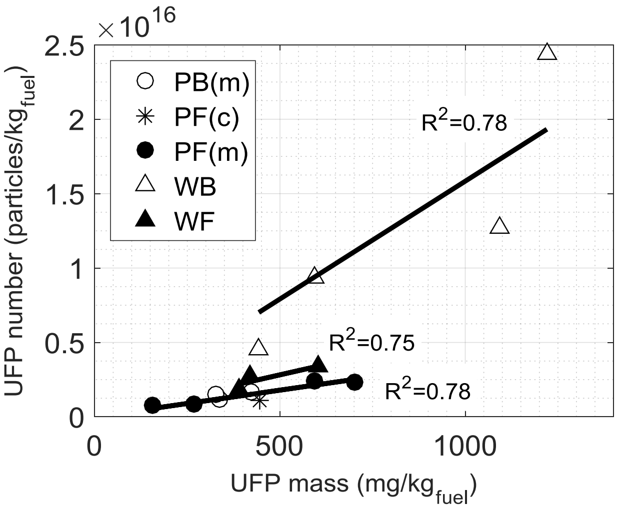

Figure 4: UFP number vs. mass emission factors. (PF: pellet stove – fir pellets PB: pellet stove – beech pellets; (m): power modulation; (c) constant heat output; WF: wood stove – fir

firewood; WB: wood stove – beech firewood)

3.3 Effects of stove operation and wood type on UFP composition

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

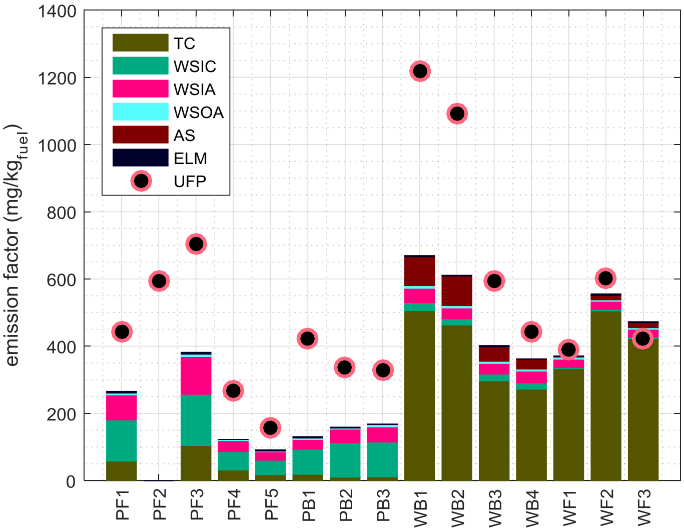

Figure 5: UFP species emission factors (mg/kg$_{fuel}$). (PF: pellet stove – fir pellets PB: pellet stove – beech pellets; WF: wood stove – fir firewood; WB: wood stove – beech firewood)

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

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

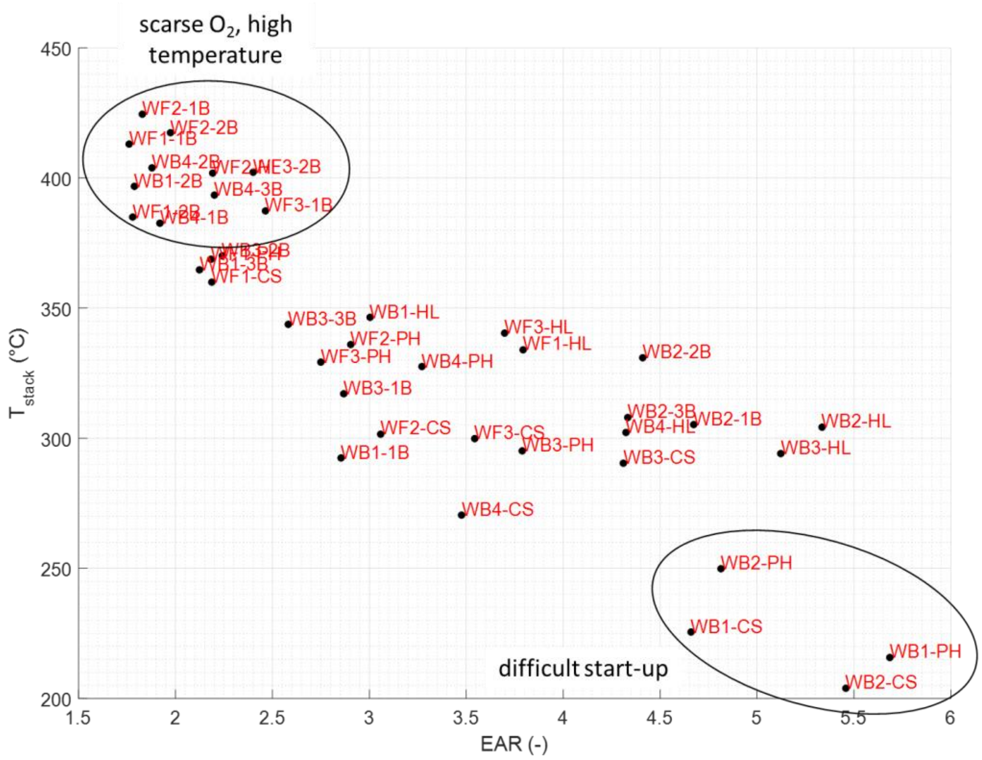

Figure 6. Per-batch average excess air ratio (EAR) vs. stack gas temperature for different test runs (PF: pellet stove – fir pellets; PB: pellet stove – beech pellets; WF: wood stove – fir firewood; WB: wood stove – beech firewood; CS: cold start; PH: pre-heating; 1B, 2B, 3B: first, second and third 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 mg/kg$_{fuel}$, range 68-265 mg/kg$_{fuel}$) than the wood stove (44 mg/kg$_{fuel}$, range 28-67 mg/kg$_{fuel}$). 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.

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

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

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

The emission factors of 8 PAHs (Phe, Ant, Flu, Pyr, BaA, Cry, BbF, BaP) are collectively referred to as Σ8PAHs. The automatically controlled and fed pellet stove has very small PAH emissions (average 52 $\mu g/kg_{fuel}$, standard deviation: 46 $\mu g/kg_{fuel}$). PF1, PF3 and PB1, corresponding to those with the highest pellet UFP mass, have relatively higher amounts of PAH detected. EFs for wood stove are orders of magnitude larger, amounting to an average of 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 beech wood burning. The lowest excess oxygen and the highest temperatures reached during fir firewood experiments hinted to very intense combustion conditions favoring the formation of PAH species. PAH fingerprints are provided in the supplementary material (Figure FSM1). The proportion of lower MW PAHs (i.e., 3- and 4- ring isomers, Phe, Ant, Flu, Pyr) in the Σ8PAHs is higher for the pellets samples, whereas wood samples are enriched in higher MW PAHs (i.e., 4- and 5- ring isomers, BaP, BbF, Cry, BaA). The PAHs measured by the study and defined by the International Agency for Research on Cancer (IARC, 2016) as group 1-carcinogenic (i.e., BaP) and group 2B-possibly carcinogenic to humans (i.e., BaA, Cry, BbF) account on average for the 85% of Σ8PAHs for the wood stove samples. The corresponding value for the two pellets samples with the highest EFs is much lower (average ~19%).

Figure 7 shows a comparison between the present study and the literature values for different types of residential heating appliances fed with different type of fuels (details and references in Table SM5 in the supplementary material). The reported emission factors are extremely variable. To reduce the effect of high and low extremes in the data only median values are compared. Even though the EFs are obtained with different sampling methodologies and for different size fractions, for mass and elements generally similar emission factors are observed for automatic pellet appliance in our study. While about three times lower TC and 60 times lower PAHs, and 3 - 5 times higher water soluble ions and anhydrosugars are found. For manually fed appliances on the other hand, 2 - 8 times lower emission factors are obtained for both mass and composition in comparison with the literature.

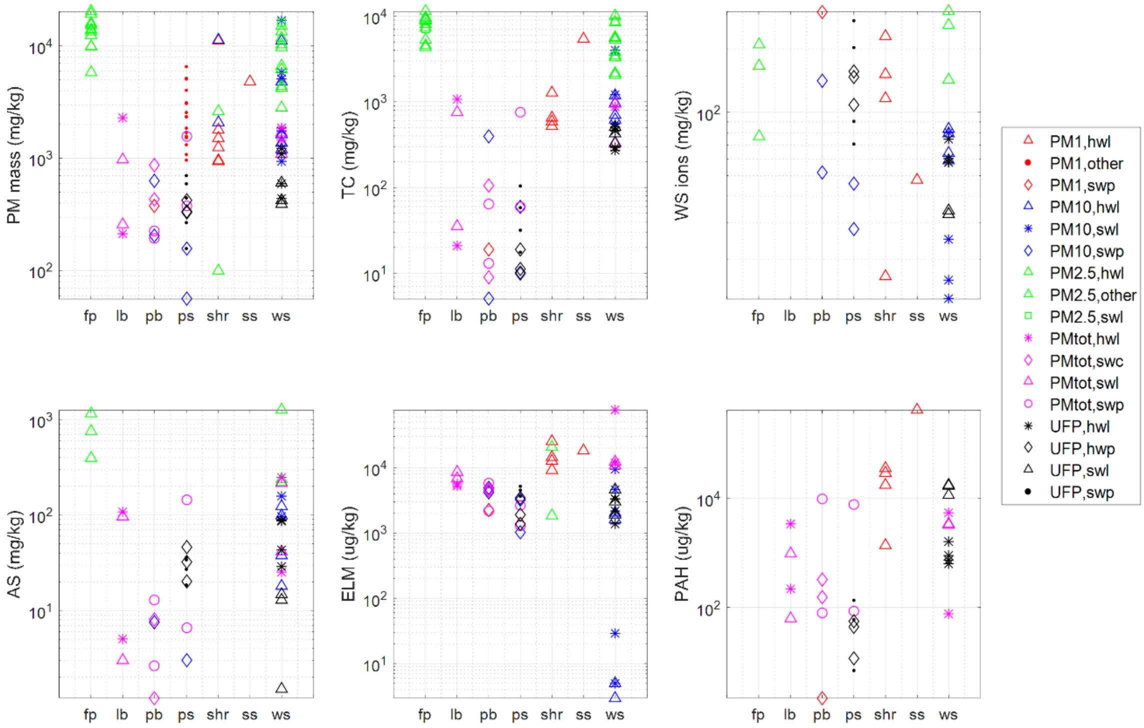

Figure 7. Comparison of literature PM mass emission factors and composition with the present study (fuel types – hwl: hardwood logs; swl: softwood logs; hwp: hardwood pellets; swp: softwood pellets; swc: softwood chips; other: various biomass) (appliance types – fp: fireplace; lb: logwood boiler; pb: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

3.4 Diagnostic ratios

PAH diagnostic ratios:

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

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

Even if not directly comparable due to different sampling methodologies, size fractions, combustion appliances and dilution conditions considered, the experimental diagnostic ratios are presented in comparison with several others found in literature (Table SM6 in the supplementary material). BbF/Flu is one of the ratios proposed as a signature factor to identify the sources of particulate PAHs in the atmosphere (Fu et al., 2010). The PM10 emission samples in the cited study have shown much higher BbF/Flu ratios (~3.7) for woody biomass burning aerosol than aerosols originating from the burning of diesel fuel and gasoline (0.047-0.050). The BbF/Flu ratio in the present study on UFP fraction ranges between 3.6-11.0 (average 6.9). Other binary diagnostic ratios reported in the literature for vehicle exhaust are ~1 and ~10 (Pyr/BaP ratios), and 0.73 and 0.5 (BaP/[BaP+Cry] ratios), respectively from gasoline and diesel vehicles, and 0.6 for Flu/Pyr ratio from generic vehicular emissions species (Ravindra et al., 2008). The corresponding average values (ranges reported in parentheses) for 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, BaP/[BaP+Cry], and Flu/Pyr. Guillon et al. (2013) report Phe/(Phe+Ant), Flu/(Flu+Pyr) and BaA/BaP ratios in the PM2.5 samples of several biomass species with averages respectively of 0.84, 0.49 and 1.46. Corresponding experimental findings in the present study are respectively 0.78 (0.61-0.88), 0.44 (0.30-0.50), and 0.61 (0.41-0.81).

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

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

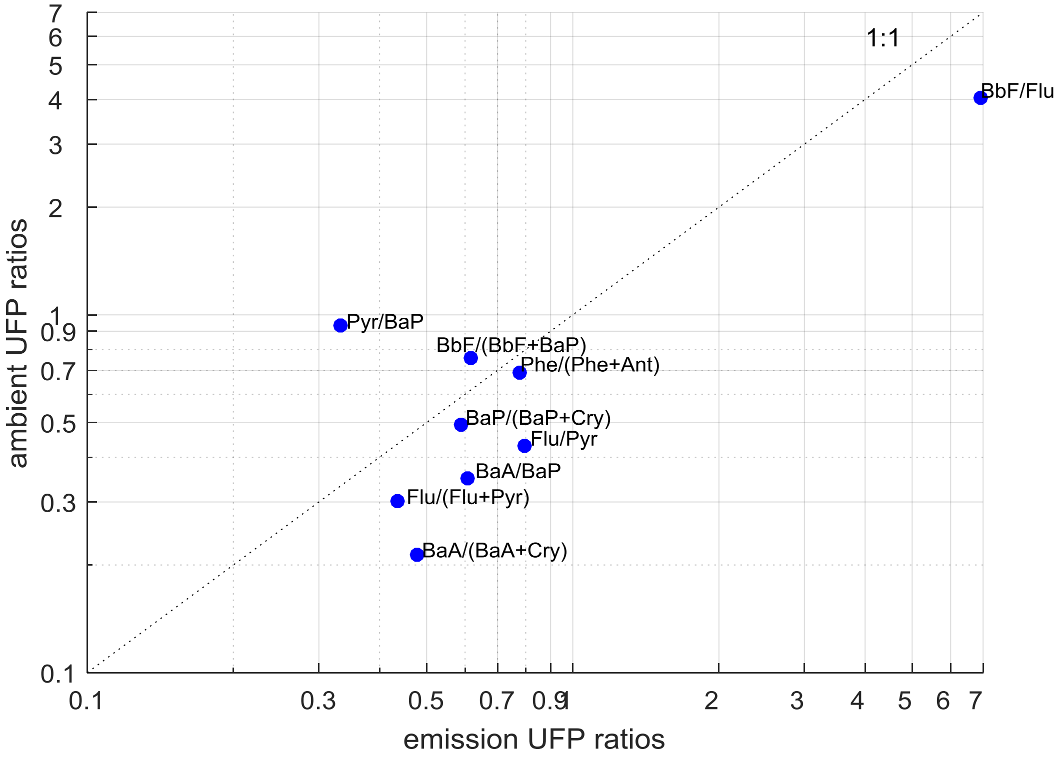

Figure 8: PAH median diagnostic ratios for emission and ambient UFP samples

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

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

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

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

5 REFERENCES

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

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

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.

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

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

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

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

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

Processing Technology 103, 51–56. doi:10.1016/j.fuproc.2011.08.020.

Fu F., Tian B., Lin G., Chen Y., Zhang J., 2010. Chemical characterization and source identification of polycyclic aromatic hydrocarbons in aerosols originating from different sources. Journal of the Air & Waste Management Association 60(11), 1309-1314.

Guillon A., Le Ménach K., Flaud P.M., Marchand N., Budzinski H., Villenave E., 2013. Chemical characterization and stable carbon isotopic composition of particulate Polycyclic Aromatic Hydrocarbons issued from combustion of 10 Mediterranean woods. Atmospheric Chemistry Physics 13, 2703–2719. doi:10.5194/acp-13-2703-2013.

IARC, 2016. IARC monographs on the evaluation of carcinogenic risk to humans. List of classifications, volumes 1–116. http://monographs.iarc.fr/ENG/Classification/index.php. (Last consulted July 2016)

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.

Leskinen J., Tissari J., Uski O., Virén A., Torvela T., Kaivosoja T., Lamberg H., Nuutinen I., Kettunen T., Joutsensaari J., Jalava P.I., Sippula O., Hirvonen M.R., Jokiniemi J., 2014. Fine particle emissions in three different combustion conditions of a wood chip-fired appliance e Particulate physico-chemical properties and induced cell death. Atmospheric Environment 86 (2014) 129-139. http://dx.doi.org/10.1016/j.atmosenv.2013.12.012.

Longhin E., Gualtieri M., Capasso L., Bengalli R., Mollerup S., Holme J.A., Øvrevik J., Casadei S., Di Benedetto C., Parenti P., Camatini M., 2016. Physico-chemical properties and biological effects of diesel and biomass particles. Environmental Pollution 215, 366-375.

Nussbaumer T., 2008. Particulate Emissions from Biomass Combustion in IEA Countries Survey on Measurements and Emission Factors. http://www.ieabcc.nl/publications /Nussbaumer_et_al_IEA_Report_PM10_Jan_2008.pdf

Obaidullah M., Bram S., Verma V.K., De Ruyck J., 2012. A review on particle emissions from small scale biomass combustion. International Journal of Renewable Energy Research 2 (1).

Ozgen S., Cernuschi S., Giugliano M., 2013. Experimental evaluation of particle number emissions from wood combustion in a closed fireplace. Biomass and Bioenergy 50, 65–74. doi:10.1016/j.biombioe.2013.01.015.

Ozgen S., Caserini S., Galante S., Giugliano M., Angelino E., Marongiu A., Hugony F., Migliavacca G., Morreale C., 2014. Emission factors from small scale appliances burning wood and pellets. Atmospheric Environment 94, 144–153. doi:10.1016/j.atmosenv.2014.05.032.

Park S.S., Sim S.Y., Bae M.S., Schauer J.J., 2013. Size distribution of water-soluble components in particulate matter emitted from biomass burning. Atmospheric Environment 73, 62-72. http://dx.doi.org/10.1016/j.atmosenv.2013.03.025.

Perrone M.R., Becagli S., Garcia Orza J.A., Vecchi R., Dinoi A., Udisti R., Cabello M., 2013. The impact of long-range-transport on PM1 and PM2.5 at a Central Mediterranean site. Atmospheric Environment 71, 176–186. doi:10.1016/j.atmosenv.2013.02.006.

Piazzalunga A., Bernardoni V., Fermo P., Vecchi R., 2013. Optimisation of analytical procedures for the quantification of ionic and carbonaceous fractions in the atmospheric aerosol and applications to ambient samples. Analytical and Bioanalytical Chemistry 405, 1123–1132. doi: 10.1007/s00216-012-6433-5.

Ravindra K., Sokhia R., Van Grieken R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. Atmospheric Environment 42, 2895–2921. doi:10.1016/j.atmosenv.2007.12.010.

Rajput P., Sarin M.M., Sharma D., Singh D., 2014. Atmospheric polycyclic aromatic hydrocarbons and isomer ratios as tracers of biomass burning emissions in Northern India. Environmental Science Pollution Research 21, 5724–5729. doi: 10.1007/s11356-014-2496-5.

Saarnio K., 2013. Chemical characterisation of fine particles from biomass burning. PhD dissertation. Finnish Meteorological Institute Contributions No. 97 FMI-CONT-97. Date: October 2013. ISBN 978-951-697-792-1 (pdf). http://ethesis.helsinki.fi

Schmidl C., Bauer H., Dattler A., Hitzenberger R., Weissenboeck G., Marr I.L., Puxbaum H., 2008. Chemical characterisation of particle emissions from burning leaves. Atmospheric Environment 42, 9070–9079. doi:10.1016/j.atmosenv.2008.09.010.

Simoneit B.R.T., Schauer J.J., Nolte C.G., Oros D.R., Elias V.O., Fraser M.P., Rogge W.F., Cass G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. Atmospheric Environment 33, 173–182.

Sippula O., 2010. Fine particle formation and emissions in biomass combustion. Report Series in Aerosol Science. No: 108. Date: March 2010. ISBN 978-952-5822-15-1 (PDF version). http://www.atm.helsinki.fi/FAAR

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.

Torvela T., Tissari J., Sippula O., Kaivosoja T., Leskinen J., Virén A., Lähde A., Jokiniemia J., 2014. Effect of wood combustion conditions on the morphology of freshly emitted fine particles. Atmospheric Environment 87, 65-76. http://dx.doi.org/10.1016/j.atmosenv.2014.01.028.

Van Loo S., Koppejan J., 2008. The Handbook of. Biomass Combustion and Co-firing. London: Earthscan.

Vicente E.D., Duarte M.A., Calvo A.I., Nunes T.F., Tarelho L.A.C., Custódio D., Colombi C., Gianelle V., Sanchez de la Campa A., Alves C.A., 2015. Influence of operating conditions on chemical composition of particulate matter emissions from residential combustion. Atmospheric Research 166, 92–100. doi:10.1016/j.atmosres.2015.06.016.

Wiinikka H., Gebart R., Boman C., Bostrom D., Nordin A., Ohman M., 2006. High-temperature aerosol formation in wood pellets flames: Spatially resolved measurements. Combustion and Flame 147, 278–293. doi:10.1016/j.combustflame.2006.08.009.

6 ACKNOWLEDGEMENTS

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Highlights:

- Ultrafine particle (dp<100nm) chemical constituent emission factors are provided

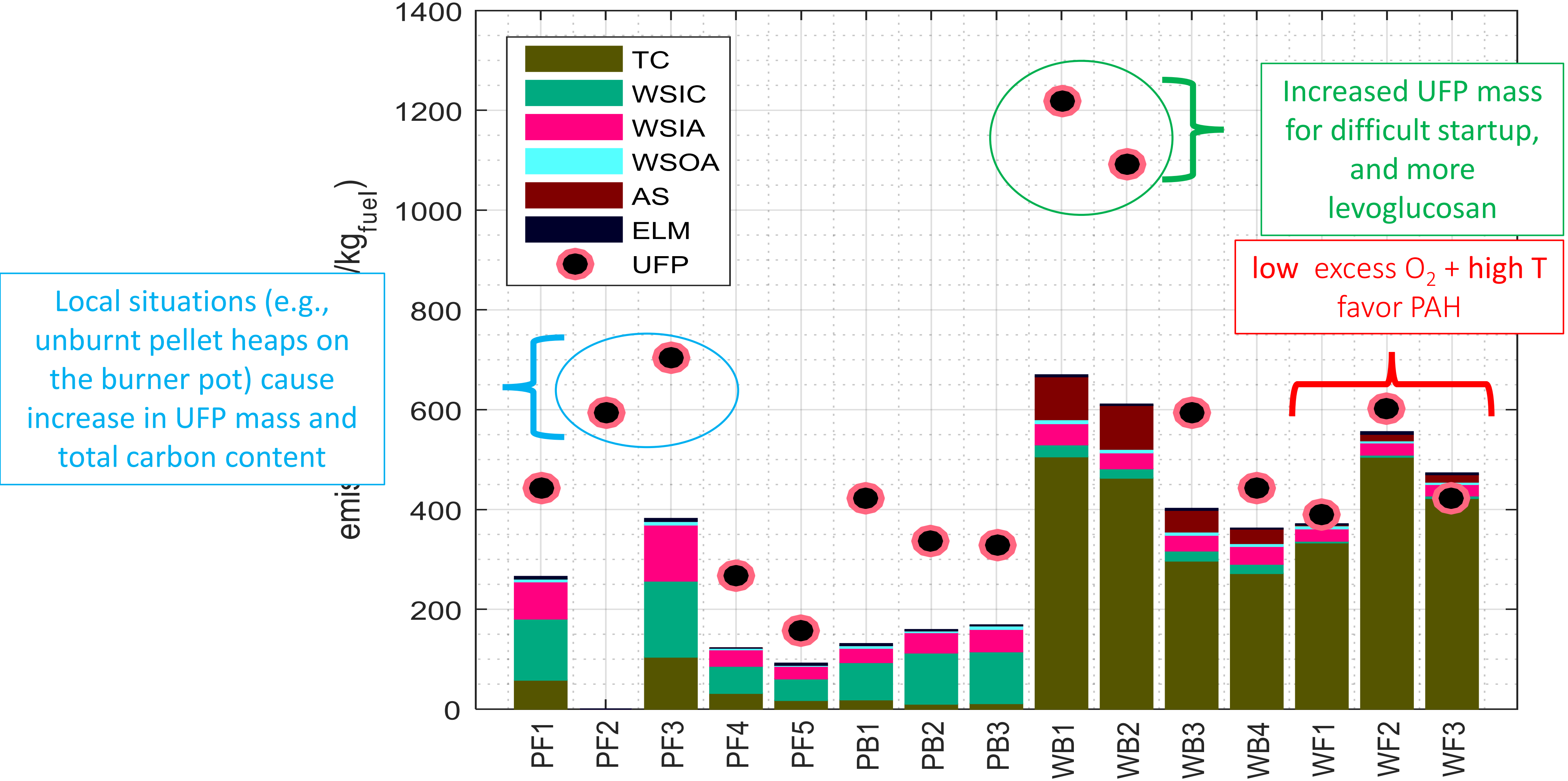
- Automatic and manually fed room heaters with two wood types are investigated

- Tests conducted with appliances working under real-world operating conditions

- Increased emissions (UFP, NOx, CO) for increased fuel ash content in the wood stove

- PAH fingerprint shifts towards more carcinogenic PAH in wood stove UFP

revised Graphical Abstract (for review)



Local situations (e.g., unburnt pellet heaps on the burner pot) cause increase in UFP mass and total carbon content

Increased UFP mass for difficult startup, and more levoglucosan

low excess O_2 + **high T** favor PAH

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