



Real-life emissions from residential wood combustion in Austria: From TSP emissions to PAH emission profiles, diagnostic ratios and toxic risk assessment

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ABSTRACT

Residential wood combustion is, besides particulate emissions, also linked to emissions of organic compounds, comprising various toxic substances such as polycyclic aromatic hydrocarbons (PAHs). Although, literature data has shown that highest emissions occur during maloperations caused by the user itself, most studies focus on lab-testing not reflecting the situation in the field. This study evaluates the real-life situation in Austria, investigating emissions of total suspended particles (TSP) and particle-bound substances of four manually operated room heaters commonly installed in people's homes. Measurements were conducted within a field measurement campaign realized in the scope of the *Clean Air by biomass* project. To evaluate the impact of the users' habit two types of combustion experiments were performed, one representing the diversity of possible maloperations and one realized under optimized conditions following a strict optimization protocol. As special focus was laid on PAHs, sampling was realized using a dilution system adapted for the use in the field. Generally, optimization lead to a clear decrease of most compounds (i.e. TSP, OC, EC, PAHs), however, emissions of the anhydrosugar levoglucosan were not affected at all. Total PAH emissions could be clearly reduced, moreover, optimization lead to a shift towards low molecular weight PAHs and thus, less toxic ones, clearly reflected by lower toxicity equivalents. Correlation analysis using the Spearman's rank method showed significantly high correlations among the individual PAH congeners, and rather low ones with other target substances.

1. Introduction

Residential wood combustion (RWC) is commonly used for heating purposes and has been identified as a major contributor to local air pollution in Austria (Caseiro et al., 2009; Kirchsteiger et al., 2020) and many other European countries as well (Bari et al., 2009; Cincinelli et al., 2019). Today it is well understood, that RWC is associated to emissions of various volatile and particulate compounds, strongly affecting the climate and human health (Manisalidis et al., 2020). However, the use of biomass for heating purposes is necessary to replace fossil fuels aiming to reach the Paris Agreement. Stationary combustion in the residential sector (NFR category 1.A.4. b) was identified as the most important emission source in Europe, with a share of 35% of total PM₁₀ emissions in 2018 (EEA, 2020). A similar situation was reported in

Austria, where 24% of total PM₁₀ emissions were caused by stationary combustion in the residential sector (NFR category 1.A.4. b) (Anderl et al., 2020). Previous studies reported that RWC emissions are strongly influenced by the design of appliances, the type of fuel, and the combustion conditions (Gonçalves et al., 2011; Orasche et al., 2012; Ozgen et al., 2014; Pettersson et al., 2011; Sturmlechner et al., 2019). Regarding Europe emissions from log wood stoves have been reported for wood types commonly used in Northern Europe (Nyström et al., 2017; Pettersson et al., 2011), in the European alpine region (Klauser et al., 2018a; Schmidl et al., 2011) and the Mediterranean area (Alves et al., 2011; Fernandes et al., 2011; Gonçalves et al., 2010). Commonly used heating devices such as room heaters or log wood stoves are often operated batch-wise under poorly optimized conditions, i.e. too high fuel load and reduced air supply, resulting in substantially fluctuating

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emissions of both particulate matter (PM) and gaseous compounds (Kistler et al., 2012; Nyström et al., 2017; Ozgen et al., 2014; Schmidl et al., 2011; Sturmlechner et al., 2019). RWC emits various toxic and carcinogenic substances including polycyclic aromatic hydrocarbons (PAHs) (Ozgen et al., 2014; Sturmlechner et al., 2019; Zhang et al., 2021), and PM including a wide variety of organic compounds such as the anhydrosugar levoglucosan (Lev) – a commonly used source marker (Simoneit et al., 1999). PAHs are generated during incomplete combustion processes, mainly emitted as complex mixtures of various congeners and some of them are of special concern, because of their known persistency, genotoxicity and carcinogenic effects (IARC, 2010). Diagnostic ratios of individual PAH congeners have been used in literature and may present a useful tool to distinguish between emission sources (Gonçalves et al., 2011; Samae et al., 2021; Tobiszewski and Namiesnik, 2012; Zhang et al., 2021). However, because of the reported intrasource variability but intersource similarity (Galarnau, 2008), PAH diagnostic ratios are widely discussed and must be interpreted carefully (Tobiszewski and Namiesnik, 2012).

Emission inventories relying on emission factors (EFs) state the basis for a profound evaluation of the influence of specific sources on air quality and may affect further implementation of mitigation strategies. EFs can be either derived by lab-testing of appliances aiming to represent close to real life conditions (Gonçalves et al., 2011; Kistler et al., 2012; Klauser et al., 2018a; Ozgen et al., 2014; Schmidl et al., 2011), or obtained from field measurement campaigns (Spitzer et al., 1998). Although the European Union strongly promotes the use of solid biomass for energy production, the data set of EFs comprising the variety of appliances and burnt fuels is limited. Due to higher costs and difficulties in experimental designs only a marginal dataset of EFs derived from field measurements reflecting the emissions which happen in real life is available.

Therefore, the present study aims to reduce the uncertainty of emission assessments and focusses on up to date EFs derived from field measurements. EFs of four manually fed appliances installed in people's homes were assessed and tested with fuels provided by the end user representing typical situations for Austria. In order to evaluate the influence of maloperations, experiments were realized under two different combustion conditions, i.e. according to the users habit and under optimized conditions. The measurement setup allowed a consecutive sampling of total suspended particles in the hot and the cooled flue gas. The main focus of this study is laid on PAH emission patterns and their change due to the optimization of combustion conditions, further linked to the overall toxicity of emissions.

2. Materials and methods

2.1. Tested appliances and fuels

The field measurement campaign was realized within the *Clean Air by biomass* project and all experiments were carried out in the time period of January to February 2018 in the municipality of Vorau, located in the Austrian region of Styria. Therefore, all devices were installed in the same region and tested during the same heating season. Combustion experiments presented in this study focus on the evaluation of emissions of four firewood room heaters (RH) produced by Austrian manufacturers. Room heaters characterized in this study are also part of the compilation of emissions given in Sturmlechner et al. (2019). All of them were of comparable design, installed in people's homes and used as additional heating source. Device 1 and 4 are currently widespread cheap to middle-price devices in the Austrian market. While device 2 is a high-priced one with a high heat storage capacity and device 3 presents a middle to high-priced device. The characteristics of tested room heaters are given in Table 1. Overall, tested devices provide an overview of the Austrian stock of log wood stoves, covering the portfolio from old devices (e.g. RH3), recently manufactured ones (e.g. RH1 and RH4) to high-end devices (e.g. RH2).

Table 1
Characteristics of tested room heaters.

	Year of construction	Nominal heat output	EN standard	Air supply
device 1 (RH1)	2013	8 kW	EN 13240	separate primary/secondary air supply, manual adjustment of both flaps possible
device 2 (RH2)	2017	8 kW	EN 13240	combined primary/secondary air control, manual adjustment of the combined flap possible
device 3 (RH3)	~1997	8 kW	ÖNORM M 7520	three different air supply possibilities: primary, secondary and air flow through the grate, manual adjustment of three different flaps possible
device 4 (RH4)	2013	7.3 kW	EN 13240	separate primary/secondary air supply, manual adjustment of both flaps possible

Experiments were carried out using fuels provided by the end-user of the respective device. Fuel types comprise commonly used fuels in Austria (i.e. spruce, larch and beech). A survey revealed that room heaters used in Austria are mainly fired with hardwood logs with a length of 0.25–0.33 m (Reichert et al., 2016a). The properties of used fuels were evaluated on the basis of representative samples according to ISO 16948 (elemental analysis), ISO 18134–2 (water content) and ISO 18122 (ash content). Fuels showed comparable composition (C (wt%): 49–51%, H (wt%): 5.9–6.3%, N (wt%): 0.1%), paired with very low ash contents (a (wt%): 0.4–0.9%), while the water content showed higher variations ranging from 6.5 to 15%.

2.2. Sampling setup and combustion experiments

Experiments were realized with an in-house developed sampling probe, which was constructed during a previous research project aiming to develop, test and validate a new technique for BaP measurements (Klauser et al., 2018c). In order to get a realistic view on ambient emissions, sampling of total suspended particle (TSP) was divided into two fractions. Sampling of both fractions was done consecutively. A scheme of the sampling system is provided in Fig. 1. TSP was sampled on quartz fiber filters in the hot flue gas flow (TSP₁₃₀ sampled at ≥130 °C) and after dilution in the cooled flue gas flow (TSP₄₀ sampled at 40 °C) promoting the recondensation of volatile species, resulting in a dilution ratio of 1:10. TSP₄₀ filters include condensable compounds. TSP₁₃₀ sampling was realized according to VDI 2066 using a heated sampling line at 130 °C which is significantly above typical dew point temperatures of flue gases (dew point: 40–50 °C), strongly depending on the air excess rates. In TSP₁₃₀ state BaP is still gaseous, whereas during TSP₄₀ conditions BaP is condensed on particulate matter. However, by additional dilution the dew point temperature of water is lowered and water condensation is avoided. In this study we solely focus on emissions of TSP and particle-bound organic compounds.

The objective of the experiments was to evaluate emissions during real-life operation and their changes due to the optimization of the combustion conditions. Each test is characterized by three consecutive batches, carried out for two combustion experiments. The duration of the combustion differed among the individual batches and sampling was always started after ignition and closure of the stove door. The first batch of each experiment represents cold start conditions, i.e. the device was at ambient temperature and ignition start-up phase was included, while the consecutive two batches represent refilling batches, i.e. hot starts with a combustion chamber already heated up. Each device was

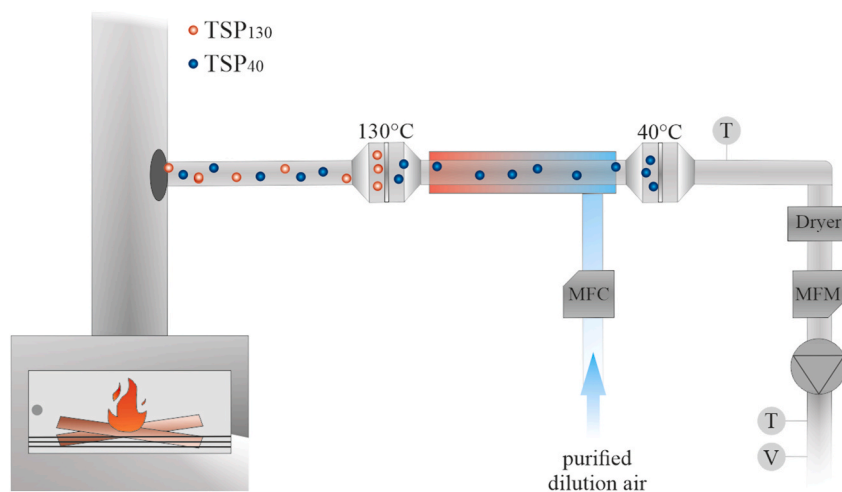


Fig. 1. Scheme of TSP sampling device, modified for field-testing purposes. Abbreviations: MFC: mass flow controller, MFM: mass flow meter, T: temperature sensor, V: flow sensor.

tested according to two different combustion experiments: 1) three consecutive batches operated according to the users habits (UH experiments), prone to be operated under poor conditions, i.e. increased fuel load and decreased air supply, improper ignition method, poor fuel quality (sometimes also burning of waste); 2) three consecutive batches with optimized combustion conditions (optC experiments), i.e. different placement, stacking and amount of fuel, restriction to proper fuel type or reduction of log size, ignition from above, optimized air supply. UH experiments represent the situation which happens in real life showing the diversity of the users' behavior, for these four comparable room heaters. A detailed descriptions of realized tests including fuel mass, air flow settings and ignition method is given in the supplement (Table A.1.). The use of waste-paper and carton during the ignition process as well as ignition from the bottom and too little air supply were most common. The number of improvements needed to reach optC experiments was different for the single experiments due to different user behavior. In the end conditions of optC experiments followed a strict protocol, i.e. ignition from above, hot starts with completely opened air supply. Refilling was defined based on the CO₂ concentrations according to the *beReal test method* (Reichert et al., 2016b). For all optC batches, measurements were continued until the CO₂ concentration reached 25% of the CO_{2,max} concentration if the absolute CO₂ concentration was already under 4%. If the CO_{2,max} concentration was below 12% and flames were extinguished at an absolute CO₂ concentration of 3%, recharging was done at this point. The end of UH batches were defined by the users' habit.

2.3. Analytical methods

TSP mass was determined gravimetrically; filter weighing was done in prior and after sampling with a precision balance (accuracy: 10⁻⁸ kg, Sartorius ME235P). Before weighing, filters were dried for 48 h in a desiccator. Chemical analysis was performed separately for both sample fractions, i.e. TSP₁₃₀ and TSP₄₀. Quantification of carbonaceous compounds, i.e. organic carbon (OC) and elemental carbon (EC) was realized by thermal-optical analysis with an OCEC Analyzer (Sunset Laboratory Inc.) and the EUSAAR 2 protocol (EN 16909:2017-06).

The quantitative determination of PAHs was performed according to DIN EN 15549:2008 using a dichloromethane and cyclohexane mixture (1/1, v/v) for extraction. Samples were analyzed using an HP6890 gas chromatograph (GC) equipped with an Agilent HP-5MS, non-polar capillary column (30 m × 0.25 mm × 0.25 μm) and coupled with an Agilent 5973 mass spectrometer (MS) with an electron ionization (EI) source and selected ion monitoring (SIM) mode. The operational

conditions of GC analysis were as follows: initial temperature 55 °C held for 1 min, increased at 25 °C/min to 320 °C and held for another 8 min. The carrier gas was helium 5.0 at a constant flow of 1.0 mL/min. A standard mixture of 18 PAHs (including the 16 U.S. EPA priority PAHs) and surrogate standards of deuterated PAHs (d₁₀-chrysene and d₁₂-benzo(a)pyrene) were purchased from Neochema (Bodenheim/Mainz, Germany). The following PAHs were quantified: fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[e]pyrene (BeP), benzo[a]pyrene (BaP), perylene (Per), indeno[1,2,3-cd]pyrene (IcdP), benzo[ghi]perylene (BghiP) and dibenz[a,h]anthracene (DBA). As PAHs lighter than Pyr tend to be preferably found in the gas phase instead of particle-bound, PAHs with mass to charge ratios smaller than 202 were not quantified.

Quantification of the monosaccharide anhydrides levoglucosan (Lev), mannosan (Man) and galactosan (Gal) was realized using high-performance anion-exchange chromatography with pulsed amperometric detection (HPAE-PAD) following the procedure presented by Inuma et al. (2009). Filter aliquots were sonicated with ultrapure water (Milli-QPlus, Millipore) and afterwards injected in a chromatographic system (Dionex ICS 3000) equipped with a CarboPac MA1 column and quantitative separation was done using an NaOH gradient (480–650 mM). No interferences with blank filters for any target compound could be quantified.

2.4. Data evaluation and calculation of emission factors

Data derived from combustion experiments was evaluated for each room heater and batch according to Klauser et al. (2018b). In brief, to evaluate ambient emissions, results for each analyte represent the sum of the hot and cooled flue gas fraction (sum of TSP₁₃₀ and TSP₄₀). The analyte mass referred to the respective flue gas volume at standard temperature and pressure (STP) and to 13% O₂ in dry flue gas. Proposed EFs are given in mg/MJ and μg/MJ, respectively. Time weighted means were calculated over three consecutive batches of one respective device normalized to the time of the respective experiment, including hot and cold starts. Median results refer to the median composition covering results of all four tested devices for either UH or optC experiment.

2.5. Statistical data analysis

Statistical evaluations were done using the statistical software R (Version 3.6.3). Correlations between respective analytes were calculated using the Spearman's rank method and correlation coefficients

were considered as significant when p-values were less than 0.05.

2.6. Calculation of BaPeq toxicity

The overall toxicity of emitted PAHs is based on the BaP equivalent (BaPeq) method recommended within the Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons by the EPA (EPA/600/R-93/089). Therefore, the EFs of individual PAH congeners were multiplied with the respective toxic equivalent factors (TEFs), which are commonly used to describe the carcinogenic potencies of individual PAHs. BaP is a widely studied compound and proven carcinogen, also listed as one of the most toxic PAHs among the 16 US EPA priority PAHs, yielding a TEF value of 1. All TEF values were evaluated relatively to the toxic potency of BaP. Within this study TEF values obtained from Larsen and Larsen were used, attributing a TEF value of 0.03 for BaA and Chr, 0.05 for Fla, 0.001 for Pyr, 0.002 for BeP, 0.1 for BbF + BkF, BghiP and IcdP; and a TEF value of 1 for BaP and 1.1 for DBA (Larsen and Larsen, 1998). Four congeners BaA and Chr as well as BbF and BkF were quantified as sum. To avoid underestimation of toxicity of those four congeners concentrations were multiplied using the higher TEF of the respective congener.

3. Results

3.1. Composition of hot and cooled flue gas samples

Sampling of the hot flue gas accounted for the main part of TSP mass (TSP_{130}), but dilution and cooling (TSP_{40}) increased to overall mass markedly. The contributions of TSP_{40} are quite similar for UH and optC experiments, showing median values of 18% and 17% of total TSP mass, respectively. Still, during optC experiments this contribution showed much higher variability and could reach up to more than 50%. As expected, hot (TSP_{130}) and cooled flue gas samples (TSP_{40}) showed quite different composition, which remain visible for UH as well as optC experiments (see Fig. A1 in the supplement). For both experiments high contributions of organic compounds were found on TSP_{40} samples. Due to the dilution and cooling step 33% (optC) or 48% (UH) of total OC are collected on the TSP_{40} filter. This process of condensation is even more pronounced when a single substance (Lev) or the sum of PAHs (PAH_{12}) is considered. 96% of total Lev concentrations and 93% of total PAH_{12} concentrations were found on the sample fraction of cooled flue gas, underlining the necessity of dilution when it comes to the determination of emissions at the ambient level. It has to be noted, that some analytes,

i.e. Lev and semi-volatile PAHs, did not show quantifiable amounts in selected TSP_{130} samples. A quite different, but expected, behavior was found for EC. The main share of EC was already collected on the hot flue gas sample (TSP_{130}). The contribution of EC on TSP_{40} samples accounted for only 1% of total EC emissions, when the median value is regarded. Nussbaumer et al. reported comparable results, showing a pronounced underestimation of particulate emissions when sampling is solely done in the chimney (Nussbaumer et al., 2008). Similar results were reported by Klausner et al. who also evaluated the emissions of room heaters, showing that dilution lead to markedly higher TSP masses (Klausner et al., 2018a). As this study aims to investigate real-life EFs, further presented results always refer to the sum of both flue gas samples (sum of TSP_{130} and TSP_{40}).

3.2. Emission factors obtained during UH experiments

EFs of TSP and the carbonaceous fractions including OC, EC, Lev and PAH_{12} were calculated for each tested device and batch as well as for the whole experiment (summing up three consecutive batches). Results obtained during UH experiments are visualized in Fig. 2a–e. A summary of EFs is listed in Table A.2. in the supplement. Highest EFs were obtained during cold starts, while consecutive hot starts showed quite similar EFs. Variations like these are quite common for emission measurements, especially during combustion experiments realized batch-wise (Gonçalves et al., 2011; Orasche et al., 2012; Ozgen et al., 2014; Schmidl et al., 2011). During UH combustion experiments time weighted means for EF_{TSP} including all batches (hot and cold starts) were in the range from 132 to 408 mg/MJ (see Fig. 2a). Highest EFs appeared during cold starts and are highlighted in blue, presenting up to 6 times higher emissions than those observed during hot starts. EFs of consecutive hot starts (black flags) showed rather low variations and also lower absolute values, which can be attributed to the higher temperature of the combustion chamber itself.

Time weighted means of EFs for OC and EC were in the range of 35.9–177 mg/MJ and 32.5–115 mg/MJ, i.e. OC emissions were slightly higher than those found for EC. Again cold starts yielded EF_{OC} values up to 9 times higher and EF_{EC} values up to 4 times higher than those observed during consecutive hot starts. One data point, i.e. hot start of device 2, was excluded from further evaluation of carbonaceous species due to an implausible result for EC, most likely due to a contamination of the filter. The share of OC to TSP accounted for 33%, while the share of EC to TSP was slightly lower, yielding 31%. The OC to EC ratio is commonly used to evaluate source contributions of ambient data. For

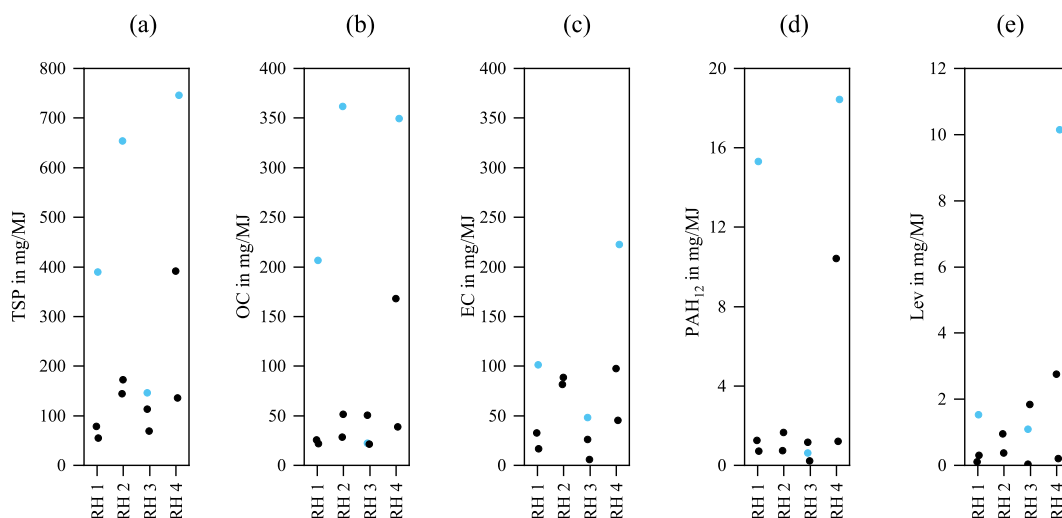


Fig. 2. a–e. Emission factors of TSP, OC, EC, PAH_{12} and Lev of three consecutive batches for four tested room heaters (RH 1–4) under UH conditions. Blue highlighted points represent emissions of cold start experiments while black highlighted points represent emissions of consecutive batches (hot starts). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

biomass combustions OC/EC ratios cover a wide range, giving more insights in the type of biomass used i.e. softwood or hardwood. For example, Gonçalves et al. reported OC/EC ratios in the range of 1.0–4.4 for hardwood and 0.9 for softwood combustions in a chimney type woodstove (Gonçalves et al., 2010). Similar OC/EC ratios were found, during combustion experiments reflecting commonly burnt fuels in Austria. Considering different burning conditions, Schmidl et al. reported OC/EC ratios ranging from 0.87 to 3.07 for hardwoods and 1.11–1.23 for softwoods, also obtained from a chimney type wood stove (Schmidl et al., 2011). The OC/EC ratios obtained in the present work varied in a wide range, with values between 0.35 and 3.47, however, the median OC/EC ratio for UH experiments (1.30) is in good agreement with those reported in literature. It is noteworthy, that OC/EC ratios obtained from biomass combustion sometimes overlap with OC/EC ratios obtained from emission measurements of other sources, e.g. traffic related emissions. Pio et al. for example, observed OC/EC ratios in the range of 0.33–0.42 for PM₁₀ and 0.29–0.37 for PM_{2.5} during tunnel measurements in Lisbon (Pio et al., 2011). This overlap of OC/EC ratios highlights the limits of using them for source apportionment.

Time weighted mean EF_{PAH12} values ranged between 0.78 and 12.5 mg/MJ. Similar to other target analytes device 1 and 4 showed highest EFs during cold starts, being up to 15 times higher than the emissions during consecutive batches. Device 2 and 3 show little fluctuation of EF_{PAH12}, with no increase of cold start emissions. We want to mention that the cold start of device 2 was not evaluated in detail according to the problems of implausible EC values, discussed before. Because of its already reported carcinogenic properties BaP is of special interest, showing EFs in the range of 50.7–653 µg/MJ. However, PAHs quantified in this study represent only a small fraction of particulate emissions, with median values ranging from 1 to 3% of TSP emissions. The EFs of individual PAHs are summarized in Table 3 and emission patterns of individual PAHs are discussed in sections 3.5. and 3.6.

The anhydrosugar levoglucosan is one marker compound which is commonly used to identify the influence of biomass combustion in ambient samples (Schmidl et al., 2008; Simoneit et al., 1999). Overall, time weighted mean emissions obtained from UH experiments were in the range from 0.53 to 3.92 mg/MJ. In most cases, EFs of Lev followed the already discussed trend with higher emissions during cold starts, representing up to 7 times higher emissions than they occurred during hot starts (see Fig. 2e). Device 3 showed less pronounced variations of EF_{Lev} and highest emissions occurred during one hot start batch. The

share of Lev/TSP and its implications for source apportionment are discussed in chapter 3.7.

3.3. Emission factors obtained during optC experiments

Results obtained for combustion experiments realized under optimized conditions (optC) are given in Fig. 3a–e. A summary of individual EFs is given in the supplement. Similar to UH experiments, EFs from optC experiments showed high variations within the consecutive batches, also caused by highest emissions during the cold start. However, the optimization of combustion conditions lead to a clear decrease of particulate emissions ranging from 86.5 to 139 mg/MJ. Generally, EF_{TSP} were up to 4 times higher during cold starts, while EFs of consecutive batches did not show pronounced variations.

Regarding carbonaceous compounds, EFs obtained during UH experiments (Fig. 2b and c) were clearly higher than EFs obtained during optC experiments (Fig. 3b and c). Considering the individual OC and EC emission, both combustion experiments (i.e. UH and optC) showed slightly higher OC emissions than those found for EC. Time weighted means of EFs for OC and EC were in the range of 34.6–61.2 mg/MJ and 3.81–63.9 mg/MJ. Again higher EFs were obtained during cold starts, with EF_{OC} values up to 8 times higher and EF_{EC} values up to 7 times higher than those observed during consecutive hot starts. EFs of device 2 and 4 showed rather low variations within the OC and EC emissions, resulting in higher EFs also during hot starts. For optC experiments the share of OC to TSP accounted 35%, while the share of EC to TSP was lower, yielding 25%. The OC to EC ratios obtained during optC experiments covered a wider range than those observed during UH experiments, ranging from 0.40 to 18.2. Although the range of OC/EC ratios expanded, both optC and UH experiments showed similar median values, i.e. 1.28 during optC experiments and 1.30 during UH experiments, which are in good agreement with previously reported ones (Schmidl et al., 2011), but still overlapping with ratios found for other sources.

Time weighted mean EF_{PAH12} values were found to be lower for optC experiments, ranging from 0.25 to 1.01 mg/MJ. Due to the optimization of combustion conditions EFs of BaP could be decreased, showing time weighted means between 10.6 and 68.5 µg/MJ. Similar to analytes already discussed, highest EFs for the sum of PAH₁₂ could be observed during cold starts. EFs from cold starts were up to 6 times higher during optC experiments than those observed during hot starts. Only results of

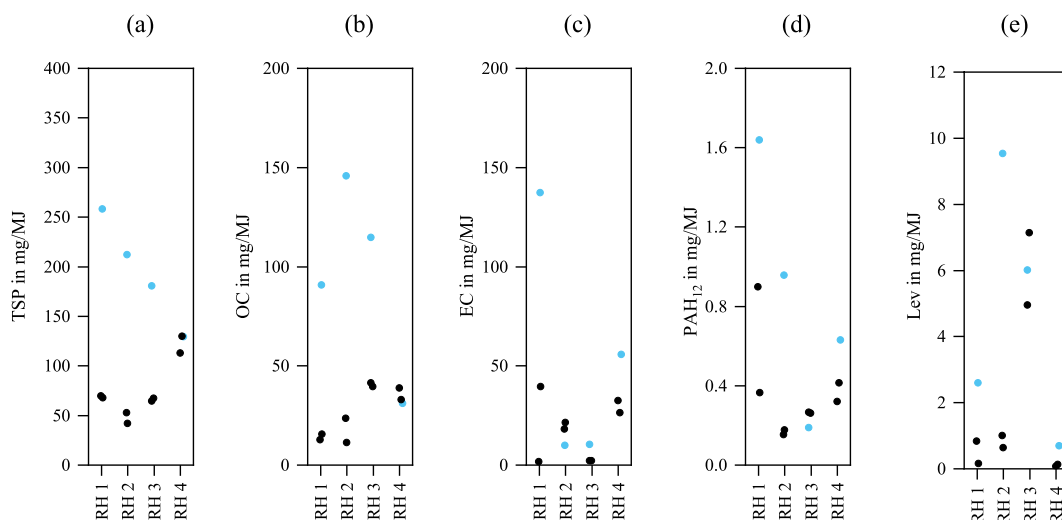


Fig. 3. a-e. Emission factors of TSP, OC, EC, PAH₁₂ and Lev of three consecutive batches for four tested room heaters (RH 1–4) under optimized combustion conditions. Blue highlighted points represent emissions of cold start experiments while black highlighted points represent emissions of consecutive batches (hot starts). Note the different y-axis compared to Fig. 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

device 3 showed less pronounced fluctuations of EF_{PAH12} and thus cold start emissions were not the highest ones. Besides that, also the total PAH content could be diminished to a maximum of 1% of TSP emissions. The EFs of individual PAHs are summarized in Table 3 and emission patterns of individual PAHs are discussed in sections 3.5. and 3.6.

Fig. 3e present the EFs of levoglucosan obtained from optC experiments and as seen before, EF_{Lev} also showed the same trend as other target analytes. Time weighted mean emissions obtained during optC experiments covered a wider range, than those from UH experiments, with EFs of Lev varying between 0.29 and 5.78 mg/MJ. Highest EFs of Lev were found during cold starts, representing up to 11 times higher emissions than they occurred during hot starts. Device 3 showed less pronounced variations of EF_{Lev} and highest emissions occurred during one hot start. Lev/TSP ratios of optC experiments and the further implications for source apportionment are discussed elsewhere (see chapter 3.7).

3.4. Comparison of TSP emission factors with literature reported for Europe

EFs determined in this study were compared with results published within the last decade using similar fuels and combustion devices (Table 2). The European emission inventory guidebook lists EFs for different technologies and compounds, given in mg/MJ while other studies refer to the amount of fuel used (i.e. mg/kg_{fuel}). A comprehensive summary presented by Vicente and Alves comprises EFs given in mg/MJ (Vicente and Alves, 2018). However, EFs reported in literature showed great variability, depending on operating conditions, fuel properties, combustion technology and the sampling procedure itself. As mentioned before, EF_{TSP} from UH experiments scatter in a wider range than those observed during optC experiments. Considering all four tested devices, the EF_{TSP} ranged from 132 to 408 mg/MJ (median: 232 mg/MJ) for UH experiments and from 86.5 to 139 mg/MJ (median: 114 mg/MJ) for optC experiments. The median values obtained for both combustion experiments are in good agreement with currently reported ones for Europe (EMEP), best described by EFs for high-efficiency stoves (average: 400 mg/MJ) and advanced/ecolabelled stoves and boilers (average: 100 mg/MJ) (EEA, 2019). To further investigate the variability of EFs from the field with ones derived from lab-testing, values were additionally compared to recent literature. However, it has to be kept in mind, that lab-testing procedures mainly focus on PM emission with a predefined cut-off, while the measurement setup used on-field

Table 2
Comparison of TSP EFs with literature data.

			Median (mg/MJ)	Min (mg/ MJ)	Max (mg/ MJ)
This study	UH	TSP	232	132	408
	optC	TSP	114	86.5	139
EMEP NFR category 1. A.4.b (EEA, 2019)	high-efficiency stoves	TSP	400		
Kistler et al. (2012)	advanced/ ecolabelled stove	TSP	100		
	manually loaded stove (8 kW) fired with logwood, 12 different wood types	PM ₁₀		20	221
Klauser et al. (2018a)	firewood room heaters (6–8 kW) fired with beech logs	TSP		57	271
	log wood stove (8 kW) fired with spruce	PM _{tot}		67	105
Orasche et al. (2012)	log wood stove (8 kW) fired with beech	PM _{tot}		93	113
	conventional stoves	PM _{tot}		340	544

Table 3
Time weighted mean EFs of PAH congeners and respective standard deviations for each device and combustion experiment. Because of implausible EC results obtained during the cold start of device 2 (RH 2*), it was excluded from further evaluation of carbonaceous compounds. Results are sorted in an ascending order of carbon atoms. Experiment is abbreviated as exp.

		Fla	Pyr	Chr + BaA	BbF + BkF	BeP	BaP	Per	IcdP	BghiP	DBA
		µg/MJ	µg/MJ	µg/MJ	µg/MJ	µg/MJ	µg/MJ	µg/MJ	µg/MJ	µg/MJ	µg/MJ
UH exp.	RH 1	1669 ± 877	1459 ± 744	1144 ± 569	859 ± 400	260 ± 122	488 ± 231	81.7 ± 39.6	231 ± 115	224 ± 115	207 ± 91.4
	RH 2 *	344 ± 142	329 ± 148	270 ± 153	193 ± 110	55.7 ± 31.5	97.6 ± 57.8	14.1 ± 8.47	54.6 ± 32.1	55.7 ± 32.6	n.a.
	RH 3	179 ± 30.4	195 ± 32.6	153 ± 28.1	84.5 ± 21.3	33.8 ± 8.87	50.7 ± 14.3	8.21 ± 2.74	27.7 ± 9.79	36.2 ± 12.1	n.a.
	RH 4	2630 ± 670	2263 ± 596	1562 ± 420	1167 ± 296	356 ± 87.3	653 ± 164	110 ± 27.7	396 ± 99.5	426 ± 124	221 ± 38.8
optC exp.	RH 1	220 ± 54.1	236 ± 56.2	152 ± 36.9	119 ± 22.6	39.9 ± 8.40	68.5 ± 13.8	11.9 ± 2.28	49.7 ± 17.6	45.2 ± 16.4	66.7 ± 19.6
	RH 2	126 ± 53.1	118 ± 48.2	72.3 ± 20.2	63.1 ± 18.5	16.5 ± 4.73	28.1 ± 8.56	3.40 ± 1.10	6.61 ± 2.38	6.07 ± 2.14	n.a.
	RH 3	79.9 ± 15.8	80.2 ± 17.2	40.1 ± 9.42	18.8 ± 4.69	7.24 ± 1.47	10.6 ± 2.64	1.54 ± 0.31	5.72 ± 1.22	8.49 ± 1.30	n.a.
	RH 4	135 ± 14.5	130 ± 13.7	62.8 ± 4.21	43.3 ± 2.24	14.5 ± 0.43	20.9 ± 0.95	2.68 ± 0.18	27.7 ± 2.02	14.3 ± 2.43	10.1 ± 0.72

quantified TSP. Schmidl et al. investigated the effect of maloperations on PM₁₀ emissions obtained for manually operated appliances typically for Austria. The authors reported a big influence of the operating procedure itself, resulting in up to 6 times higher emissions due to possibly wrong type and amount of fuel and air flow settings (Schmidl et al., 2011). An evaluation of PM₁₀ emissions of fuels commonly used in Austria and other mid-European countries, has been done by Kistler et al. using a manually fired log wood stove. Although, this study refers to TSP measurements, emissions were found to be comparable to previously found PM₁₀ emissions (20–221 mg/MJ) by Kistler et al. (2012). Emission measurements of firewood room heaters using beech logs have been realized by Klauser et al. TSP emissions for manually fed appliances (57–271 mg/MJ) reported by Klauser et al. covered TSP emissions found during experiments with optimized operating conditions (Klauser et al., 2018a). Orasche et al. investigated, among others, emissions from a manually fed log wood stove fired with beech and spruce logs, both fuels are commonly used in Austria. Besides the comparable emissions (PM_{tot}: 67–105 mg/MJ for spruce and 93–119 mg/MJ for beech), the authors also reported higher values during cold start conditions, which is consistent with the results obtained in this study (Orasche et al., 2012). All studies reported high variability of particulate emissions, but results obtained for UH experiments in this study mark the upper range found. Nussbaumer et al. evaluated particulate emissions from different combustion devices in IEA countries. PM EFs obtained from a dilutions sampling method were found to be higher, conventional wood stoves showed values ranging from 340 to 544 mg/MJ, which are partly overlapping with highest EFs found during UH experiments (Nussbaumer et al., 2008). Highest emissions and pronounced fluctuations can be attributed to the fact that the current study quantified TSP emissions accompanied by the real-life situation. Although, standardized lab-testing does not entirely reflect emissions like they occur in the field, comparable results showed, that they cover an essential range.

3.5. Detailed evaluation of individual PAH emissions

For individual PAHs no distinct difference of cold vs hot start conditions was observed and, thus, presented values refer to the time weighted mean composition within three consecutive batches (including hot and cold starts). As PAHs presented in this study were quantified from the particulate fraction, 2- and 3- ring congeners, which are primarily found in the gas phase, were not quantified. Highest emissions of BaP were obtained during UH experiments and yielded median emissions of 293 µg/MJ, while a clearly lower median value of 24.5 µg/MJ was observed for optC experiments. Presented median values comprise results from all four tested appliances derived within either the UH or optC experiments. Petterson et al. focused on the emissions of wood stoves realized under two operation modes (i.e. normal conditions and closed air inlets and moist fuel). BaP emissions obtained under both operation modes showed similar variations, in the range of 16–300 µg/MJ (Petterson et al., 2011), overlapping with results found in this study. In contrast to that, Orasche et al. investigated PAH emissions from log wood stoves realized under optimal conditions. As expected, BaP emissions reported by Orasche et al. (12–17 µg/MJ for spruce and 9–11 µg/MJ for beech) were clearly lower than those obtained here, i.e. in field measurements, even during optC experiments (Orasche et al., 2012). These results show that maloperations substantially increase the burden of PAHs. To estimate real-life emissions for all PAHs analyzed, time weighted means including all three batches (hot and cold starts) are presented in Table 3. A trend of decreasing EFs with number of condensed rings can be observed, i.e. highest EFs were found for 4-ring congeners (2607 µg/MJ for UH, 321 µg/MJ for optC experiments), followed by EFs of 5-ring congeners (1128 µg/MJ for UH, 101 µg/MJ for optC experiments) and lowest EFs were reported for 6-ring congeners (283 µg/MJ for UH, 22.6 µg/MJ for optC experiments).

In order to evaluate the correlation among individual PAH congeners and also with other quantified analytes correlation coefficients using the

Spearman's rank were calculated. Correlation coefficients are listed in Table 4 and were considered as significant with a p-value less than 0.05. With exception of DBA, most PAHs showed significantly high correlations among each other. Lower correlations of individual congeners with DBA may be caused by the diminished data set for DBA, because only device 1 and 4 emitted DBA concentrations above the limit of detection. Especially high correlations found for Chr + BaA, BbF + BkF, BeP, BaP, Per and IcdP may indicate common formation pathways. Comparison with previous studies is rather difficult because the number of PAHs analyzed differs among studies, thus results were additionally compared to ones obtained from natural sources. Vicente et al. evaluated, among others, the amount of PAHs emitted from wildfires in Portugal (Vicente et al., 2017). They also reported high correlations for lighter PAH congeners such as Fla, but also for DBA. Overall, PAH₁₂ emissions showed a good correlation ($r = 0.75$) with TSP emissions, while the correlations of individual congeners to TSP were rather low. Furthermore, Table 4 also lists the correlations between individual PAHs with other analytes quantified in this study. PAH₁₂ showed a higher significant correlation to EC ($r = 0.70$) than observed for OC ($r = 0.59$), further PAH₁₂ to Lev emissions did not show a significant correlation ($r = 0.11$).

3.6. PAH emission profiles and diagnostic ratios

Consistent PAH profiles could be observed for almost all batches within either the UH or the optC experiment. Fig. 4 presents the share of individual PAHs to PAH₁₂ emissions and the respective relative standard deviations for all four tested devices under both combustion experiments ((a) UH experiments and (b) optC experiments). During both combustion experiments, highest shares were found for Fla and Pyr, while lowest shares were obtained for Per. The comparison of the emission profiles of both combustion experiments visualizes a shift towards low molecular weight PAHs (LMW PAHs) due to optimized conditions. During UH experiments (Fig. 4a) the share of 4 ring congeners accounted for 65%, while it increased to 73% during optC experiments. Even though, previous studies investigated a different number of PAHs, similarities of dominating LMW PAHs in emissions of residential wood combustion could be observed (Orasche et al., 2012; Petterson et al., 2011; Samae et al., 2021). Among 5-ring congeners, BbF + BkF showed the highest share of PAH_i/PAH₁₂ emissions (12% for UH experiments and 11% for optC experiments), followed by the share of BaP/PAH₁₂ accounting for a maximum of 10% of total PAH₁₂ emission during UH and 9% during optC experiments. In this respect no marked change occurred. Although the number of optimizations differed among devices, it lead to a pronounced reduction of PAH₁₂ emissions to 11% during optC experiments compared to UH experiments, while emissions of the highly toxic BaP could be decreased to 8%. Thus, the optimization of combustion conditions lead to a shift of PAH emission patterns, pictured in Fig. 4c. Relative emissions of LMW PAHs to total PAH content increased while the share of high molecular weight PAHs (HMW PAHs), i.e. 5- and 6-ring congeners showed ambivalent behavior. Although the total emission of PAH₁₂ decreased, the share of 5-ring congeners was not affected at all, showing neglectable changes (see Fig. 4c). A similar situation can be observed for 6-ring congeners. During UH experiments similar contributions of IcdP and BghiP could be observed within the respective devices, while the shares varied within optC experiments. It has to be noted, that only device 1 and 4 showed quantifiable concentrations of DBA.

The overall toxicity was evaluated on the basis of BaP_{eq} emissions. BaP_{eq} showed considerable differences for both experiments, i.e. UH and optC. BaP_{eq} values of UH experiments, did not only show higher absolute values yielding 0.02–2.37 mg/MJ, they were also characterized by higher variations. OptC experiments revealed a shift to higher emissions of LMW PAHs, resulting in lower BaP_{eq} values accompanied with less pronounced variations, ranging from 0.01 to 0.30 mg/MJ. These results clearly highlight, that the optimization of combustion

Table 4

Spearman rank correlation matrix between individual PAHs and other quantified analytes. Correlations with coefficients ≥ 0.80 with a p-value < 0.05 were considered as significant (bold).

	TSP	Lev	OC	EC	Fla	Pyr	Chr + BaA	BbF + BkF	BeP	BaP	Per	IcdP	BghiP	DBA	PAH ₁₂
TSP	1.00														
Lev	0.44	1.00													
OC	0.79	0.53	1.00												
EC	0.71	0.07	0.48	1.00											
Fla	0.83	0.23	0.68	0.71	1.00										
Pyr	0.79	0.23	0.66	0.66	0.98	1.00									
Chr + BaA	0.65	0.03	0.48	0.67	0.90	0.93	1.00								
BbF + BkF	0.58	-0.07	0.41	0.66	0.86	0.87	0.96	1.00							
BeP	0.58	-0.07	0.39	0.62	0.87	0.89	0.97	0.98	1.00						
BaP	0.55	-0.09	0.40	0.64	0.85	0.88	0.96	0.98	0.99	1.00					
Per	0.67	0.00	0.50	0.60	0.85	0.88	0.96	0.97	0.99	0.99	1.00				
IcdP	0.73	0.06	0.59	0.67	0.88	0.90	0.96	0.95	0.96	0.96	0.95	1.00			
BghiP	0.73	0.05	0.56	0.68	0.89	0.91	0.93	0.90	0.92	0.91	0.95	0.99	1.00		
DBA	0.60	0.63	0.62	0.54	0.77	0.77	0.81	0.79	0.81	0.80	0.79	0.91	0.88	1.00	
PAH ₁₂	0.75	0.11	0.59	0.70	0.97	0.98	0.97	0.94	0.96	0.94	0.95	0.96	0.95	0.81	1.00

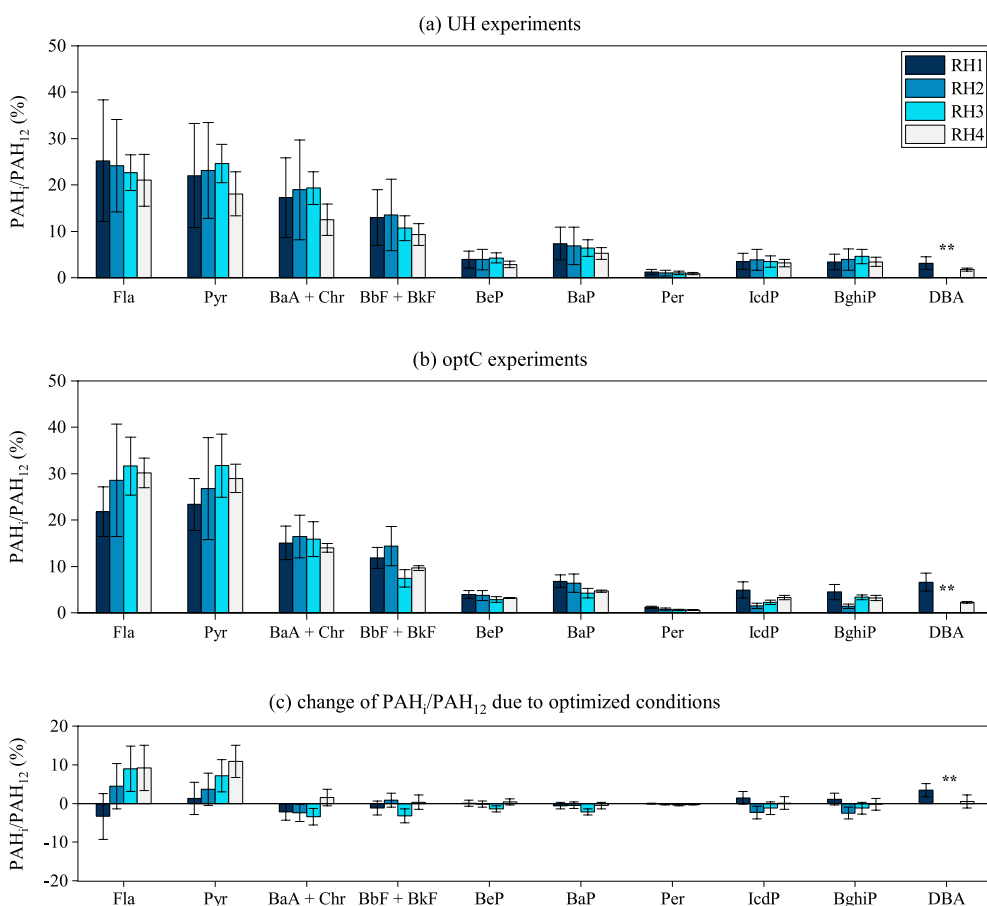


Fig. 4. a-c. Emission patterns of individual PAHs of UH experiments (a) and optC experiments (b). Error bars represent the relative standard deviation within the consecutive batches. No quantifiable DBA concentrations (highlighted with *) could be obtained for device 2 and 3. The change of PAH_i to PAH₁₂ partitioning due to optimization of combustion conditions is shown in Fig. 4c, in this case error bars display the standard deviations of changes. Results are sorted in an ascending order of carbon atoms.

conditions not only results in a distinct decrease of PAH₁₂ emission, but also to a shift to PAHs with lower toxicity. Quite similar shares of BaP to BaP_{eq} were observed during UH experiments and optC experiments, accounting for 54% and 55%, respectively. Although, the sample size of DBA was smaller, the contributions of DBA to the BaP_{eq} emissions showed similar results, yielding 23% and 24% for UH and optC experiments.

Diagnostic ratios of specific PAHs are widely used to identify the influence of possible emission sources such as biomass or fossil fuel combustion, i.e. traffic related emissions (Galarneau, 2008; Tobiszewski and Namiesnik, 2012). Besides that, diagnostic ratios also show intra-source variabilities and intersource similarities (Galarneau, 2008).

However, most emission sources do not show unique PAH signatures and ambient air contains a complex mixture of PAHs, which probably undergo a variety of atmospheric processes. Still the evaluation of PAH diagnostic ratios of specific emission sources may help to characterize the relevant sources. Generally, congener ratios observed in this study scatter in a wider range than previously reported ones. Fla/(Fla + Pyr) ratios were in the range of 0.47–0.54 for UH experiments and 0.47–0.52 for optC experiments. Ratios of IcdP/(IcdP + BghiP) showed an even more pronounced variation ranging from 0.39 to 0.59 for UH experiments and 0.44–0.60 for optC experiments. Both congener ratios are used to distinguish between source types and are in good agreement with those reported by Orasche et al. and Klauser et al. who investigated

emissions of beech and spruce combustion (Klauser et al., 2018b; Orasche et al., 2012). The ratios observed for IcdP/(IcdP + BghiP) during the experiments done by Klauser et al. were slightly higher than those observed in this study (Klauser et al., 2018b). As BaP and BeP show a different behavior in photodegradation, the congener ratio BaP/(BaP + BeP) evaluates if particles did already undergo atmospheric degradations. Literature data suggests, that atmospheric degradations leads to BaP/(BaP + BeP) ratios below 0.5 while freshly emitted particles show congener ratios around 0.5 (Tobiszewski and Namiesnik, 2012). UH experiments showed median values for BaP/(BaP + BeP) of 0.64 while slightly lower median congener ratios of 0.61 were found for optC experiments. As the present study solely evaluates freshly emitted particles, we recommend that also BaP/(BaP + BeP) ratios above 0.5 have to be considered as so. For comparison Table 5 also lists congener ratios of the combustion of fuels with similar elemental composition but different combustion type. Congener ratios obtained in this study are in the range of recently reported ones for biomass combustions, however, the pronounced variability of each ratio emphasizes that single ratios are not representative for sources emitted under different circumstances. Comparing these ratios with those listed by Galarneau show a rather blurring transition for Fla/(Fla + Pyr) ratios of various sources. In the case of IcdP/(IcdP + BghiP) no overlapping of ratios can be observed, however, the IcdP/(IcdP + BghiP) ratio reported for wood combustion marks the lower range compared to additionally listed ones. This might be attributed to the fact, that all other studies investigated the PAH congener ratios of biomass commonly used in Europe, while Galarneau focused on fuels typically used in the US. This leads to the conclusion, that the evaluation of diagnostic ratios and emissions profiles for commonly used combustion systems in the area of interest is crucial to reveal the impact of different sources.

3.7. Levoglucosan emissions and its implications for ambient data

Emissions of levoglucosan are of interest as several source apportionment tools are based on this tracer substance. As technology evolves this factor has to be checked and updated on a regular basis to avoid under- or overestimations in source apportionment. Figs. 2e and 3e present the EFs of levoglucosan obtained for both combustion experiments. EF_{Lev} showed highest EFs during cold starts, but overall emissions remain quite similar for both combustion experiments (i.e. UH and optC experiments), ranging from 0.53 to 3.92 mg/MJ and 0.29–5.78 mg/MJ, respectively. This leads to a clear difference of the Lev to TSP contributions. During UH experiments the maximum share of Lev to TSP yielded 3% while a shift to higher shares was observed during optC experiments (up to 11%). It has to be noted, that during UH experiments the cold start of device 2 was excluded from evaluation due to

implausible EC results. If we would consider the Lev/TSP ratio of this batch too, the maximum share observed during UH experiments would shift to 8%. Median Lev/TSP shares (0.6% for UH experiments and 1% for optC experiments) are much lower. Comparison with literature data is difficult, as results are only reported for Lev/PM₁₀ ratios. For example, the evaluation of manually fired log wood stoves yielded a share around 5% of Lev/PM₁₀ (Schmidl et al., 2011), while average concentrations obtained from tiled stoves accounted for 4.1% for beech and 15.1% for spruce of total particle mass (Schmidl et al., 2008). The contributions of Lev to particulate emissions obtained from different combustion devices scatter in a wide range, and so do conversion factors used for source apportionment. Schmidl et al. evaluated Lev/PM₁₀ ratios of predominantly used biomass types in Austria yielding a conversion factor of 10.7 (Schmidl et al., 2008). An even higher conversion factor (20) was obtained for combustion experiments realized with manually operated log wood stoves (Schmidl et al., 2011). Based on the maximum Lev/TSP ratios observed in this study, conversion factors of 37 and 9.5 were obtained for UH experiments and optC experiments. Based on median values these conversion factors would be much higher, reflecting the different reference to TSP instead of PM₁₀. Furthermore, it has been reported that technological development towards higher combustion efficiency, results in lower emissions of many compounds. For example, automatically operated systems underlying more controllable conditions, tend to emit lower amounts of particles and anhydrosugars (Orasche et al., 2012; Schmidl et al., 2011). As these varying conversion factors may have considerable impact on the application of macro-tracer derived source apportionment, the Lev emissions of different combustion devices have to be evaluated in more detail, to decrease the uncertainty coming along with the use of conversion factors.

Besides Lev, also Mannosan (Man) and Galactosan, are emitted by the combustion of cellulosic material (Schmidl et al., 2008). All three anhydrosugars are known to be emitted in different proportions, strongly depending on the used fuel and, besides the OC/EC ratios, the ratios of mentioned isomers are used to distinguish between types of biomass (i.e. hardwood or softwood). Although Man is known to be emitted in much lower concentrations, we found quantifiable amounts for all tested room heaters. Both combustion experiments showed clearly different Lev/Man ratios, the median Lev/Man ratio obtained during UH experiments was 6.5, while the median ratio for optC experiments was clearly higher, yielding 12. The Lev/Man ratios reported by Schmidl et al. for manually fired log wood stoves varied between 14 and 17 for hardwoods, while they were lower for softwoods (2.5–3.5) (Schmidl et al., 2011). Comparing these results with those obtained earlier by Schmidl et al. assumes a higher contribution of hardwoods. This aligns with results of the survey reflecting the Austrian situation, proposing that room heaters are predominantly fired with hardwoods

Table 5
PAH diagnostic ratios presented for this study including results published previously.

			Fla/ (Fla + Pyr)	IcdP/ (IcdP + BghiP)	BaP/ (BaP + BeP)
This study	room heater	UH experiments	0.47–0.54	0.39–0.59	0.53–0.66
		optC experiments	0.47–0.52	0.44–0.60	0.48–0.65
Orasche et al. (2012)	log wood stove under optimal conditions	spruce ^b	0.50–0.52	0.52–0.54	0.62–0.65
		beech ^b	0.49–0.50	0.53–0.57	0.61–0.64
Klauser et al. (2018b)	firewood room heater	beech firewood, only experiments without catalyst	0.44–0.52	0.72–0.79	0.50–0.60
Gonçalves et al. (2011) ^a	woodstove	golden wattle ^b	0.38–0.46	0.53–0.59	–
		eucalypt ^b	0.44–0.46	0.53–0.58	–
Galarneau (2008) ^c	wood combustion		0.51 ± 0.16	0.42 ± 0.18	–
	diesel vehicles		0.40 ± 0.05	0.19 ± 0.13	–
	gasoline vehicles		0.52 ± 0.13	0.32 ± 0.11	–
	coal combustion		0.57 ± 0.21	0.48 ± 0.29	–

^a For better comparison only fuels with similar elemental composition were considered.

^b Range includes hot and cold start conditions.

^c Mean values and standard deviations calculated from EFs reported in US EPA (US EPA, 1998).

(Reichert et al., 2016a).

4. Summary & conclusion

To reflect real-life emissions, field measurements were realized using appliances installed in people's homes, fed with the fuel provided by the end user. EFs obtained during UH experiments scatter in a wider range and were found to be higher than those observed for optC experiments. Variations of TSP, OC, EC, Lev and PAH₁₂ EFs were mainly caused by higher emissions during cold starts, no matter of combustion experiment. However, a clear decrease due to the optimization of combustion experiments was observed especially for TSP, OC, EC and PAH₁₂, while the emissions of Lev were not affected at all.

In order to evaluate the overall toxicity of RWC emissions, special focus was laid on PAHs and the contribution of individual congeners. PAH patterns of both combustion experiments showed a trend of decreasing EFs with increasing number of condensed rings.

The optimization of combustion conditions lead to a reduction of absolute PAH₁₂ emissions and also to a shift in PAH emission patterns. Relative emissions of LMW PAHs to the PAH₁₂ content mostly increased while the share of HMW PAHs showed ambivalent behavior, i.e. the share of 5-ring congeners only showed neglectable changes, while 6-ring congeners showed decreasing shares. The overall toxicity of PAH emissions was evaluated on the basis of BaP equivalents, clearly highlighting that it can be reduced due to optimized combustion conditions.

Although, the emissions of biomass combustion vary in a wide range, optimization lead to a distinct decrease of the majority of target analytes accompanied by lower overall toxicity. These results show that user training is of similar importance as changes in technology, because maloperations may counteract technological improvements. The high variations found for biomass combustion show, that EFs are only representative when a diversity of maloperations and appliances is considered. However, it is quite difficult to draw a firm conclusion about their effects on source apportionment, possible reduction measures or emission inventories. This would require an even more extensive evaluation of EFs obtained from field measurements, which is accompanied by much higher costs and effort as ones obtained from lab-testing.

Author statement

Bernadette Kirchsteiger: Conceptualization, chemical analysis, writing and original draft preparation; Florian Kubik: chemical analysis; Magdalena Kistler: review and editing; Rita Sturmlechner, Harald Stressler and Manuel Schwabl: field measurements, testing procedure, gravimetric analyses of filter material, review and editing; Anne Kasper – Giebl: Conceptualization, writing, review and editing. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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