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Fuel xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Fuel

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

On-line analysis of organic emissions from residential wood combustion with single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS)

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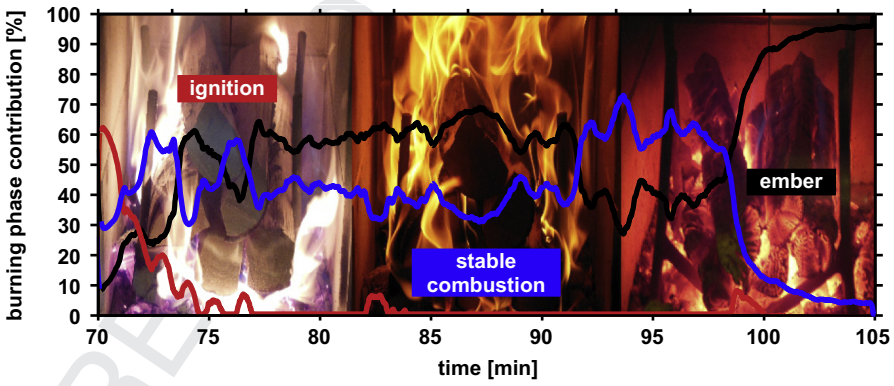
HIGHLIGHTS

- Examination of VOC, IVOC and SVOC emission from masonry heater with air staging.
- High time resolution allows to monitor short combustion events.
- Semi-quantification of VOC and IVOC for three common firewoods.
- Highest organic emissions in first two of six batches.
- Molecular signature of gas phase for each burning phase.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 4 June 2015
Received in revised form 9 March 2016
Accepted 10 March 2016
Available online xxxx

Keywords:
Masonry heater
VOC
Air staging
Batch combustion
Burning phase

ABSTRACT

A study about the temporal variation of organic emissions from a modern wood log fired masonry heater was carried out with different gas analysis techniques: single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS) for real-time analysis of volatile (VOC), intermediate-volatile (IVOC) and semi-volatile organic compounds (SVOC), and a gas analyser system for gaseous components CO_2, CO, NO_x and organic gaseous carbon (OGC, quantified by flame ionisation detector). The emissions of three in Europe common types of firewood (beech, birch and spruce) were investigated by combustion of six consecutive batches of 2.5 kg each over 4 h. Batchwise emissions and temporal variations during combustion were discussed. Emission factors over the whole combustion cycle for OGC, VOC and IVOC were right up to one order of magnitude lower than in many previous studies due to latest improvements of air staging technology in wood log fired masonry heaters, whereas CO and NO_x remained comparable. Regarding each combustion experiment, more than 50% of the total intensity of the mass spectra occurred during the combustion of the first two batches. Moreover, the molecular signatures of burning phases ('ignition', 'stable combustion' and 'ember') were examined by using non-negative matrix factorisation (NMF) and

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http://dx.doi.org/10.1016/j.fuel.2016.03.036
0016-2361/

principal component analysis (PCA) in sequence. Marker substances for wood or biomass combustion, such as phenolic species or furan derivatives, exhibited highest relative abundance during 'stable combustion', whereas 'ember' is distinctly characterised by polyunsaturated hydrocarbons, such as benzene or naphthalene, through pyrosynthesis; in 'ignition', secondary decomposition products dominated. Nevertheless, highest quantitative emissions always occurred during 'ignition' at the beginning of each batch, followed by the phases 'ember' and 'stable combustion'.

1. Introduction

According to Directive 2009/28/EC, the Commission of the European Union fixed targets for its member states to reach a mean percentage of 20% renewable energy of the final energy consumption in the whole European Union until 2020. The directive was preceded by the decision to pursue an incorporative energy and climate policy, declared in the European climate package from 2007. A potential way to produce energy from renewable source is the combustion of wood. In 2010, wood amounted for 38%, 50% and 30% of renewable energy consumption in the three most heavily populated EU countries Germany, France and United Kingdom [1]. Previous studies has been shown that wood combustion contributes significantly to indoor and outdoor air pollution, especially to ambient air fine particle concentrations [2–4], known for inducing adverse health effects [5–7]. In addition to particulate emissions, wood combustion is also a significant source of volatile organic compound (VOC) emissions which are known for their deleterious effect on human health and as precursors for atmospheric secondary organic aerosol formation [8–10]. With ongoing improvements on wood stoves, the composition of released VOC might change qualitatively as well as quantitatively and has to be evaluated consistently to support toxicological studies and to keep atmospheric models updated.

Most of previous studies about wood combustion-related VOC used adsorbents [4,11–13] or gas sampling bags [14] for thermodesorption gas-chromatography (TD-GC) to obtain integrated results of one combustion experiment. However, these techniques are time consuming and cannot gather the dynamics of wood combustion. Thus, time-resolved information was predominantly achieved by Fourier-transform infra-red spectroscopy (FTIR), proton-transfer-reaction mass spectrometry (PTR-MS), or resonance-enhanced multiphoton ionisation time-of-flight mass spectrometry (REMPI-TOFMS) [15–21]. Moreover, pyrolysis of small amounts of wood with evolved gas analysis was carried out to examine volatile decomposition products of wood or its major polymeric components lignin, cellulose and hemicellulose [22–24].

This following study was carried out in the framework of the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE) at the University of Eastern Finland (UEF). The project HICE investigates causes and mechanisms of environmentally influenced diseases for a deeper understanding of impacts of anthropogenic aerosols, such as wood combustion aerosols, on human health. Innovative in-vitro human lung tissue models were exposed to these aerosols. State-of-the-art analytical techniques are applied for comprehensive, non-targeted analyses of small molecules in anthropogenic aerosols and on different biological levels (transcriptome, proteome, metabolome, toxicological parameters).

As a part of the chemical analysis in HICE, we describe on-line measurements with single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS) to characterise VOC, intermediate-volatile (IVOC) and semi volatile organic compounds (SVOC) from a modern masonry heater, which was equipped with the novel technique of air staging [25] and fuelled with three types of commonly used firewood (beech, birch and spruce). The potential of SPI-TOFMS to examine and monitor short-term events in combustion/pyrolysis experiments with low detection limits, in particular of wood combustion [26], has been previously demonstrated [27,28]. Due to a different selectivity to PTR-MS and low fragmentation rates, SPI-TOFMS augments the knowledge from previous studies in that field and enables to unravel the molecular composition of wood combustion-derived VOC to SVOC.

In the following, batch-to-batch emission factors (EF) of CO, NO_x, OGC and 10 selected VOC/IVOC are presented and compared with EF from stoves of previous studies. Finally, the high time resolution is used to figure out consequences of occasionally inappropriate ignition and qualitative differences of emission in three burning phases by applying non-negative matrix factorisation (NMF).

2. Materials and method

2.1. Experimental setup

2.1.1. Stove setup

The combustion experiments were performed with a modern masonry heater (*Hiisi 4*; Tulikivi Ltd., Finland) which was equipped with an upright enclosed firebox, double glass window door and controlled combustion air supply. In general, the combustion process is relatively fast and combustion chamber temperatures are relatively high in this type of heat-retaining fireplaces. The heat released during the combustion process is retained in the surrounding massive soapstone structure and released slowly as supplemental heat.

Flue gases were led from the firebox to the upper combustion chamber and then downwards through side ducts into the stack. The stack was placed below a hood, and draught was regulated with two dampers. The target value for the pressure in the stack was (12.0 ± 0.5) Pa below ambient pressure.

The combustion air was distributed as primary air flow through the grate (less than 20% of total air supply), as secondary air flow above the fuel batch through small rifts in the firebox (about 45%) and as window flushing air (about 35%). The advantages of this type of air staging in batch combustion appliances are reduced gaseous and particulate organic emissions compared to conventional non-staged combustion [25,29].

2.1.2. Fuel characterisation

Two hardwoods (beech, birch) and one softwood (spruce), which are widespread as fuel for residential heating, were tested. Analysis of the wood concerning calorific properties, water content and elemental composition was conducted by an external laboratory based upon international standards (Table 1).

2.1.3. Combustion procedure

In total, eight combustion experiments were carried out including two beech ('beech1' and 'beech2'), four birch ('birch1', 'birch2', 'birch3' and 'birch4') and two spruce experiments ('spruce1' and

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Table 1
Elemental composition and properties of the log woods.

Property	Unit[a]	Method	Birch	Beech	Spruce
Moisture	%	DIN EN 14774-2	7.2	9.0	7.4
Ash at 550 °C	% (w/w)	DIN EN 14775	0.69	1.3	0.58
Carbon	% (w/w)	DIN EN 15104	51.0	50.3	52.0
Hydrogen	% (w/w)	DIN EN 15104	6.0	5.8	5.9
Nitrogen	% (w/w)	DIN EN 15104	0.40	0.36	0.36
Oxygen	% (w/w)	Calculated	41.9	42.3	41.1
Sulphur	% (w/w)	DIN EN 15289	0.006	0.037	0.009
Chlorine	% (w/w)	DIN EN 15289	<0.005	<0.005	0.005
Potassium	mg/kg	DIN EN ISO 17294-2	500	1330	640
Lower heat value	kJ/kg	DIN EN 14918	18140	17,790	18,640

[a] Related to dry basis.

'spruce2'). Due to an intermittent shutdown of the gas analyser system, experiment 'birch3' was excluded from EF calculations. Each experiment lasted for four hours, during which six batches of wood were burned. In the first batch, ten logs were laid cross wise (0.23 kg each). On top of the logs 150 g of smaller wood pieces were placed as kindling. Ignition of the first batch was always done from the top by a basic lighter fuelled with butane. Batches 2–6 consisted of five logs (0.5 ± 0.05) kg each. The weight of each batch was (2.50 ± 0.20) kg, so in each experiment the total amount of wood was 15.0 kg.

Apart from the duration of the first batch the combustion procedure was consistent for all wood species. For 'beech2' and each birch experiment, the first batch lasted for 30 minutes because of faster burning, while for 'spruce1', 'spruce2' and 'beech1' the duration was 35 min. In all cases batches 2 to 6 were burned for 35 min and after batch 6 no more wood was refilled. The remaining ember was stoked and the secondary air channels were closed according to the official instructions given by the stove manufacturer. The embers went on glowing until a total time of four hours was reached (35 min with 'beech2' and birch, 30 min with spruce and 'beech1'). As combustion experiments were done in consecutive days, the cooling of the combustion appliance was enhanced with a blower between the experiments, in order to cool the stove down to room temperature.

2.2. Instrumentation

2.2.1. Bulk gas and temperature analysis

Flue gas composition including carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2) and nitrogen oxides (NO_x) were measured continuously by a gas analyser system (ABB, Cemas). The sum emissions of organic gaseous compounds (OGC) were quantified by a flame ionisation detector (ABB, Multi-FID 14), which was calibrated against propane. All gaseous emissions were measured directly from undiluted stack gas through an insulated and externally heated (180 °C) sampling line. Flue gas temperature was determined from the stack right after the masonry heater gas outlet with a K-type thermocouple.

2.2.2. Single photoionisation time-of-flight mass spectrometry (SPI-TOFMS)

VOC, IVOC and SVOC of the emission were analysed by a time-of-flight mass spectrometer (TOFMS; *Compact Reflectron Time-of-Flight Spectrometer II*, Kaesdorf Geräte für Forschung and Industrie) with single-photon ionisation (SPI) at 118 nm (photon energy of 10.49 eV). SPI refers to a soft ionisation technique, thus leading to molecular ions and low fragmentation. Every compound with an ionisation energy below the photon energy becomes ionised whereby the ionisation efficiency strongly depends on the compound class [30]. VUV-photons of 118 nm were generated by multiple frequency increases of the fundamental radiation of 1064 nm of a Nd:YAG-laser (*Spitlight 400*, Innolas GmbH, Krailling, Germany). During the experiments, D_3-toluene (mass-to-charge ratio m/z = 95; toluene methyl-D3, 98% purity, Cambridge Isotope Laboratories, Inc.) was constantly added as internal standard leading to a concentration of 0.911 ml/m^3 (=0.911 ppmv) in the raw gas. The following mass spectra were related to the intensity of m/z 95, which represents 0.806 ppmv due to its isotopic composition and a small yield of the tropylium ions. The flue gas was sampled at 220 °C with stepwise increasing temperature to 245 °C to prevent condensation. At 230 °C a glass fibre filter, which was replaced before every new combustion experiment, was installed to hold back particles and to approximate an atmospheric gas-particle partitioning of SVOC. For a more detailed description of the instrumental setup see also supplemental material S1.

2.3. Non-negative matrix factorisation (NMF)

Positive or non-negative matrix factorisation (PMF/NMF) can be used to combine measured variables according to their abundances in the experiment to identify single processes, e.g. to determine burning phases in batchwise wood combustion [20]. NMF is an iterative technique and partitions a non-negative n-by-m matrix M in to a n-by-k matrix W and a k-by-m matrix H. The number of factors k is the only predefined variable. W and H are computed by an alternating least-squares algorithm to minimise the functional

$$f(\mathrm{W},\mathrm{H}) = \frac{1}{2}\|\mathrm{M} - \mathrm{WH}\|_F^2 \quad (1)$$

where $\|X\|_F$ computes the Frobenius-norm of a non-negative matrix X:

$$\|X\|_F = \sqrt{trace(X^T \cdot X)} \quad (2)$$

Thus the product of W and H is called a non-negative facterisation of M, although WH has not to be equal to M. NMF requires no further input variables than k, so the iteration starts with random initial values W_0 and H_0 for W and H, respectively. To avoid convergence into a local minima, W_0 and H_0 are optimised before running the NMF by using a multiplicative algorithm, which is more sensitive towards the convergence criterion [31].

Many studies in atmospheric science refer to the algorithm by Paatero and Tapper named positive matrix factorisation (PMF) [32], but PMF and NMF can be regarded as interchangeable [31].

3. Results and discussion

3.1. Emissions of 4 h combustion cycle

The masonry heater emitted approximately one order of magnitude lower concentrations of VOC than combustion appliances in

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Table 2
EF of OGC, CO, NO_x in mg/MJ and 10 single VOC and IVOC in μg/MJ (dry basis).

	OGC	CO	NO_x	PRP	AA	VAC	BTD	BENZ	TOL	STYR	IND	NAP	MNAP
beech1	27.7	1496	106.0	1568.3	3889.8	95.6	275.4	1607.6	202.4	78.7	50.6	326.0	22.5
beech2	22.4	1372	117.6	1068.0	2563.2	61.8	179.9	1096.1	123.7	50.6	33.7	213.6	11.2
birch1	13.4	2152	106.1	788.3	1075.0	33.1	170.9	909.6	115.8	44.1	27.6	215.0	22.1
birch2	18.7	1602	104.5	529.2	804.9	38.6	198.5	766.3	148.8	55.1	22.1	176.4	22.1
birch4	15	1153	104.7	622.9	1405.7	44.1	198.5	766.3	137.8	55.1	27.6	176.4	33.1
spruce1	44.9	1291	83.1	4662.0	8632.0	305.8	1078.3	2376.6	777.9	203.9	166.3	627.7	91.2
spruce2	19.6	1663	86.9	1073.0	2832.6	85.8	295.1	1201.7	236.1	69.7	32.2	279.0	26.8

PRP = propene; AA = acetaldehyde; VAC = vinylacetylene; BTD = butadiene; BENZ = benzene; TOL = toluene; STYR = styrene; IND = indene; NAP = naphthalene; MNAP = methylnaphthalene.

previous studies without air staging, while emissions of CO and NO_x were not affected (Table 2).

In our experiments, CO levels cover a range from 20 g/kg ('birch4') to 38 g/kg ('birch1'). NO_x concentrations were almost constant in all experiments, viz. 1.5 g/kg ('spruce1' and 'spruce2')–2.1 g/kg ('beech2'), and lie within the range of literature data. OGC refers to a quantity which represents the sum of volatile organic compounds and varies the most by a factor of three, from 0.23 g/kg ('birch1') to 0.79 g/kg ('spruce1'). OGC results of this study agree well with data from Lamberg et al. [33] and Tissari et al. [34], who both burned birch wood in a modern masonry heater with improved secondary air supply. Lower emissions of OGC compared to results from Nuutinen et al. [25], who used a similar modern masonry heater with air staging, can be explained by the longer experiment time in our study during which the combustion chamber temperature increased and OGC declined (Table S2). Regarding the different types of wood, birch wood features the lowest emission of OGC, but the limited number of experiments does not allow generalising this result.

By using SPI-TOFMS together with an internal standard, semi-quantification of single compounds is principally possible (supplemental material S3.2.). The EF of VOC and IVOC follow the same trend as OGC from this study and are also one order of magnitude lower than concentrations from previous studies [11,13,25,35]. For example, propene, which is one of the most abundant compounds, is determined as 9.6–14.3 mg/kg for birch wood, whereas Tissari et al. [35] measured even 210 mg/kg wood (Table S3).

3.2. Time-resolved emission

3.2.1. Emission of single wood batches

Batchwise emissions were compared by averaging measured quantities (OGC, CO, NO_x and intensities of m/z) over each batch including the char-burning phase at the end and calculating their proportion to the overall emission (Fig. 1); batchwise EF can be found in the supplemental material (Table S4). The highest peak intensities can be observed during the first two batches, whereas from the third batch down to char-burning the intensity of most m/z decreases steadily. Thus, the number of batches affects the integrated emission of one batch combustion experiment. For example, the combustion procedure of Nuutinen et al. [25] included only three batches and no char-burning, leading to higher emission factors for OGC. The combustion of remaining char at the end of the experiment reveals the smallest fraction of the overall organic emission.

To find out which measured concentrations are significantly higher in one batch or two batches when compared to the whole 4 h combustion cycle, a single and double Grubbs' Outlier Test [36] for six batches (excluding char-burning) were performed. It turned out that mathematical outliers are maxima and mainly occur in the first two batches. In six of seven experiments, CO was released in significantly higher concentrations than in other batches. Nevertheless, CO emissions occur for 30–70% during the last 30 min in the char-burning phase when considering the whole combustion cycle. By contrast, NO_x emissions were more comparable from batch to batch and much lower during char-burning. Apart from 'birch1' and 'birch2', OGC emissions were always significantly enhanced in the first two batches, but not for every detected VOC, IVOC or SVOC. In five of the eight experiments, m/z 40 (allene, propyne), 66 (cyclopentadiene), 78 (benzene), 92 (toluene), 94 (phenol), 128 (naphthalene), 118 (indane), 104 (styrene), 102 (phenylacetylene), 168 (dibenzofuran, methylsyringol), 178 (phenanthrene, anthracene), 180 (vinyl-syringol, coniferyl alcohol, fluorenone) and 202 (pyrene/fluoranthene) are significantly more abundant in the first two batches. Except coniferyl alcohol and methylsyringol, each one of these compounds does not belong to the group of wood-specific emissions and are more general combustion products. The absence of oxygen in the molecules or low O/C ratio as well as low H/C ratio indicate secondary formation by pyrolysis of precursors such as phenolic species [37,38], or by pyrosynthesis in flames [39,40].

One of the most abundant hydrocarbons is benzene, which is released with a proportion of 51–63% of the whole emission only during the first batch. Many studies about the pyrolysis of pure cellulose/hemicellulose, and lignin or lignin monomers by thermal analysis are available, but none of them observed a considerable release of benzene below 900 K [24,38,41]. Therefore, high benzene emissions during first batches are likely caused by pyrosynthesis, although the temperature inside the combustion chamber is the lowest during the whole combustion procedure. Additionally, this hypothesis is supported by the temporal trend of the smallest PAH naphthalene (m/z 128), which is also formed by pyrosynthesis [42] and runs proportionally with benzene in all batches of all experiments (correlation coefficient $r = 0.98$). Moreover, the two VOC toluene and benzene play an important role for atmospheric scientists: Their ratio toluene-to-benzene (tol/benz) can be used as photochemical clock due to higher reaction rates of toluene with OH-radicals compared to benzene as well as for source apportionment studies. Jordan et al. state that tol/benz is lower than 1 for biomass burning in residential areas [43], but for the examined stove with air staging this limit seems too rough since tol/benz of all batches and wood types show a mean ratio of 0.17 (median: 0.15; 1st quartile: 0.10; 3rd quartile: 0.22). This fact might become more relevant when prospective atmospheric studies of source apportionment are conducted in residential areas of developed countries.

Three of four birch experiments show significantly enhanced intensities of several m/z in the third batch compared to the 4 h combustion experiment. One explanation for significantly elevated intensities in the third batch might be that the combustion residue from the previously burned logs is lower than for other woods. Consequently, there might be not enough combustion residues to ignite the new logs efficiently so that the emission profile is more comparable to the first batch. Moreover, experiment 'spruce1' attracts special attention because the first batch account for approximately 70% of the total intensity. 'Spruce1' is compared

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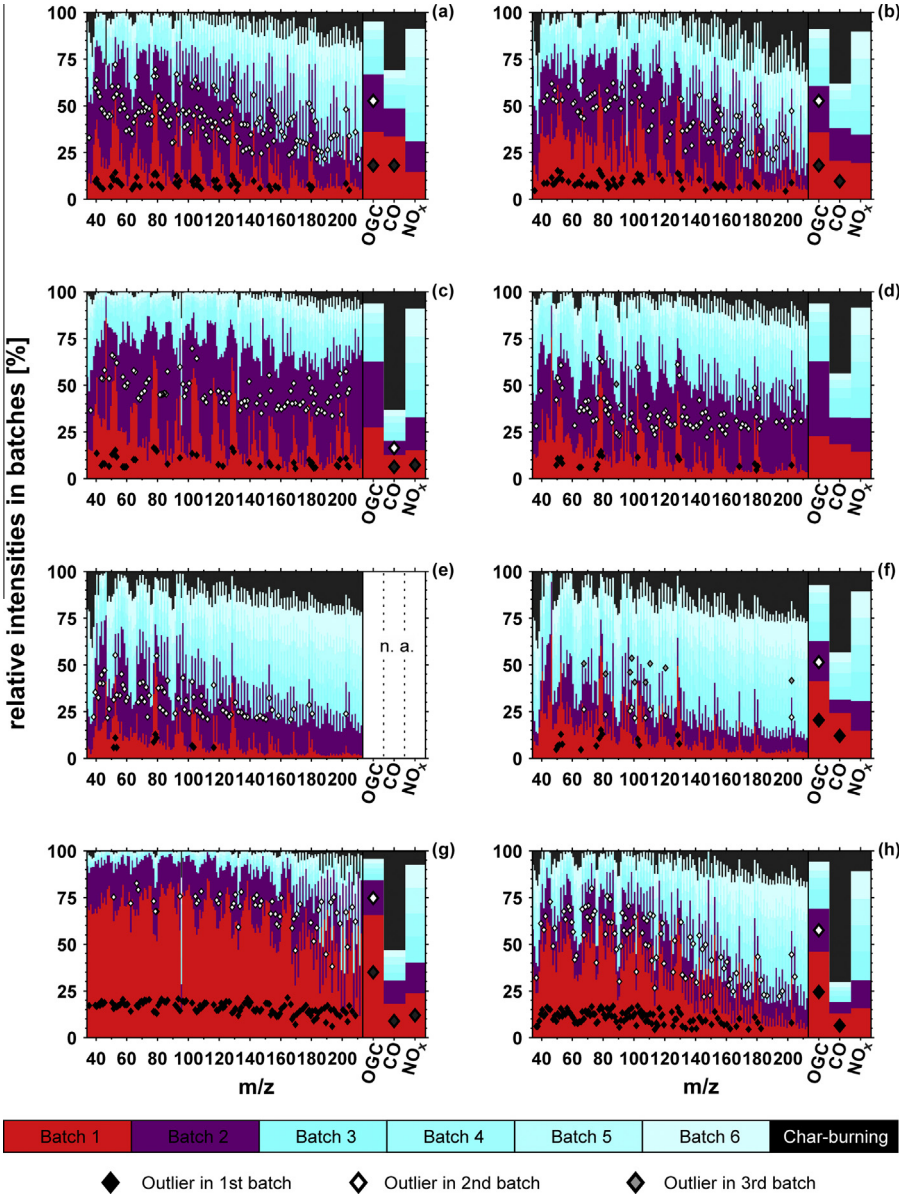

Fig. 1. Proportions of *m*/*z*-intensities, OGC, CO and NO_x in batches and char-burning phase for (a) 'beech1', (b) 'beech2', (c) 'birch1', (d) 'birch2', (e) 'birch3', (f) 'birch4', (g) 'spruce1', and (h) 'spruce2'. For single and double Grubbs' Outlier Test, only batches one to six, but no char-burning were considered. Significantly enhanced intensities are marked with diamonds in black, white and grey for batch numbers one, two and three, respectively.

to the second spruce experiment 'spruce2' and discussed more in detail in the following Section 3.2.2.

3.2.2. Proper vs. interrupted ignition

SPI-TOFMS provides on-line combustion monitoring with temporal resolution of 1 s. Together with flue gas temperature, CO, NO_x and OGC, this benefit can be used to analyse temporal variations of the combustion process and to examine the differences between the experiments 'spruce1' and 'spruce2' (Fig. 2).

First of all, the peaks of organic compounds during the first minute of the first batch can be assigned to the combustion of the fast-burning kindlings utilised to ignite the whole batch. Regarding the flue gas temperature of both experiments, it is striking that their trends show different behaviour. For the temperature in 'spruce2' (Fig. 2b), the typical bell-shaped curve [35] can be observed, which is linked to combustion phases [20]. At the beginning, the flue gas temperature rises when the logs are ignited, followed by peaking during harsh and stable combustion and finally resulting in a slight decline. On the contrary, in experiment 'spruce1' the temperature drops between 5 min and 8.5 min before rebounding (Fig. 2a). In this time, OGC and CO grow dramatically, while CO_2 decreases, which all indicate incomplete combustion. The same observation can be made to a lower extent between 18 min and 23 min when the flue gas temperature twice reaches a plateau. However, increased concentration of OGC is not defrayed in equal proportions of all organics, which can be monitored by benzene (*m*/*z* 78, pyrosynthesis), guaiacol (*m*/*z* 124, lignin-monomer), coniferyl alcohol (*m*/*z* 180, lignin-monomer of soft wood) and levoglucose none/hydroxymethylfurfural (*m*/*z* 126, both decomposition products of (hemi-)cellulose) in Fig. 2c. When the flue gas temperature drops, a smouldering-like phase begins with a disproportional increase in primary decomposition from lignin and carbohydrates. The ratios of the peak intensities of the three primary decomposition products to benzene grow from 5 min on and spike between 18 min and 23 min. It seems that the combustion progress is disturbed and releases intensified primary decomposition products.

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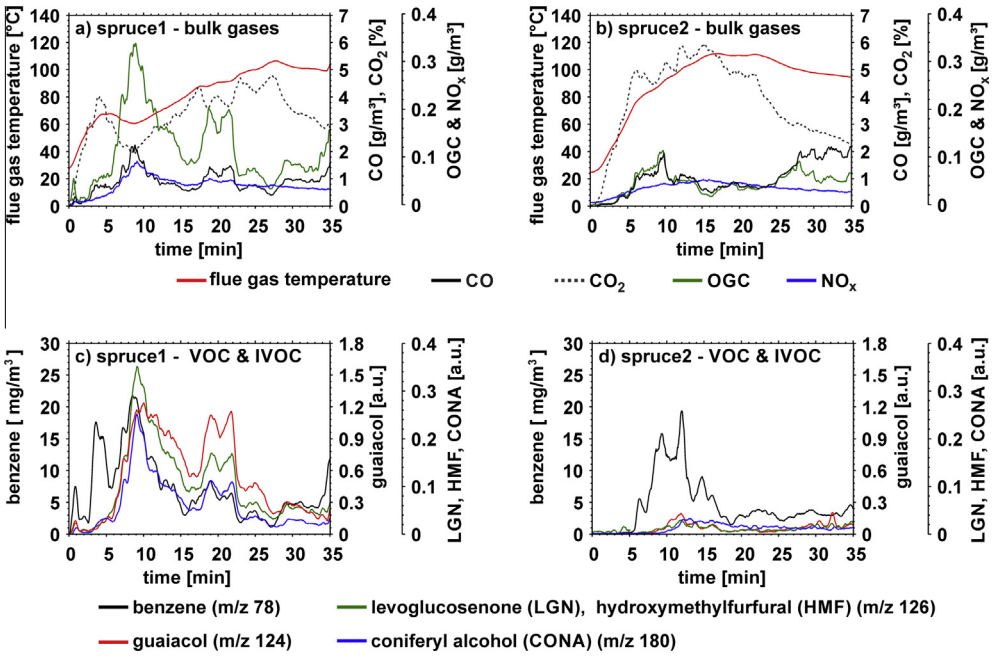

Fig. 2. First batch temporal trends of experiments 'spruce1' (left) and 'spruce2' (right) for most abundant gaseous emission (top), and VOC/IVOC (bottom).

Comparing the first batch of 'spruce1' and 'spruce2', benzene is only enhanced 1.6-fold, whereas *m/z* of guaiacol, levoglucose none/hydroymethylfurfural and coniferyl alcohol are 10-fold, 26-fold and 5-fold increased. OGC, which represents all VOC and IVOC, is only 2.5-fold increased. Moreover, the failed ignition of the first batch affects the results of the whole combustion experiment, elucidated by highest emission factors for OGC and all semi-quantified components. Only minor elevation is observed for NO_x during the temperature drop compared to other experiments. Experiment 'spruce1' is the only one where such a smouldering phase during ignition obviously occurred.

3.2.3. Determination of burning phases and their molecular signature

The wood combustion passes through different burning phases, thus the emission profile even changes distinctly with time during one batch and even covers a dynamic range up to four orders of magnitude. Each *m/z* features its highest abundance at the beginning of each batch, while the intensity maxima tend to decrease with ongoing batches. Within one single batch, two different temporal trends for *m/z* traces are perceived: The first group of *m/z* diminish steadily, whereas the second group has its maximum at the beginning as well, but passes through a minimum and increases again towards the end of the batch. Mainly *m/z* of 78 (benzene), 128 (naphthalene), 54 (butadiene), 52 (vinylacetylene), and 42 (propene) belong to the second group, remaining *m/z* to the first group, which indicates that the combustion passes through different phases.

Additional to the particulate phase analysed by aerosol mass spectrometry [20], wood combustion burning phases can also be determined by the gas phase through SPI mass spectra and subsequent NMF. Only even *m/z* were selected to diminish the original data because wood consists mainly of carbon, hydrogen and oxygen, which can only form molecules of even masses and thus even-numbered molecular ions. For NMF, a three factor solution was preset to obtain results analogue to PMF results by Elsasser et al. [20].

From NMF, two matrices were obtained: the first one represents the absolute factor contribution, the second set contains the factor loadings. Burning phases 'ignition', 'stable combustion' and 'ember' were identified by their temporal trends, previous burning phase identification by OGC, CO_2 and CO can be found in the supplemental material S5.1. The relative factor contributions and factor loadings for 'spruce2' in% were calculated and exemplarily illustrated in Fig. 3a and b. So far, the contribution of single organic compounds to these phases has not been investigated yet. On that account, molecular patterns of each burning phase were figured out from 24 obtained factor loadings by principal component analysis (PCA) [44]. Before starting the PCA based upon covariance, NMF factor loadings were normalised to their respective total intensity and subsequently centred.

The first two principal components (PC1 and PC2) explain 82.7% and 10.9% of the total variance. In the score plot, burning phases are well separated on the positive *x*-axis (ember) and in the second (stable combustion) and third quadrant (ignition). However, clustering of wood types cannot be observed, therefore the burning conditions, e.g. a proper ignition, seems to be more important for the examined combustion appliance.

In positive direction PC1 is exclusively loaded with *m/z* corresponding to unsaturated hydrocarbons, e.g. benzene (*m/z* 78), naphthalene (*m/z* 128), vinylacetylene (*m/z* 52) and allene/propyne (*m/z* 40), which are mainly formed by pyrosynthesis. Thus, the positive loading of PC1 can be regarded as a convenient representative for the glowing of charcoal-like combustion residues.

Compared to 'ember', 'ignition' and 'stable combustion' are only separated by PC2. The positive loading of PC2 can be predominantly assigned to C2- to C5-carbonyls (*m/z* 44, 58, 72, and 86), crotonaldehyde (*m/z* 70), hydroxyacetone (*m/z* 74) and the furan-derivates C2-furan/furfural (*m/z* 96), furfurylalcohol (*m/z* 98), methyl-furfural (*m/z* 110) and hydroxymethylfurfural (*m/z* 126). Lower factor loadings in PC2 occur for phenol-derivates guaiacol (*m/z* 124), methyl-guaiacol (*m/z* 138), eugenol (*m/z* 164), catechol (*m/z* 110) and coniferylalcohol/vinylsyringol (*m/z* 180). Furans, carbonyls and phenolic species refer to specific decomposition products of (hemi-)cellulose and lignin, therefore the positive loading of PC2 can be regarded as primary decomposition. Conversely, PC loadings in negative direction contain mainly unsaturated hydrocarbons, such as propene (*m/z* 42), propyne/propadiene (*m/z* 40), butadiene (*m/z* 54), toluene (*m/z* 92), isoprene (*m/z* 68),

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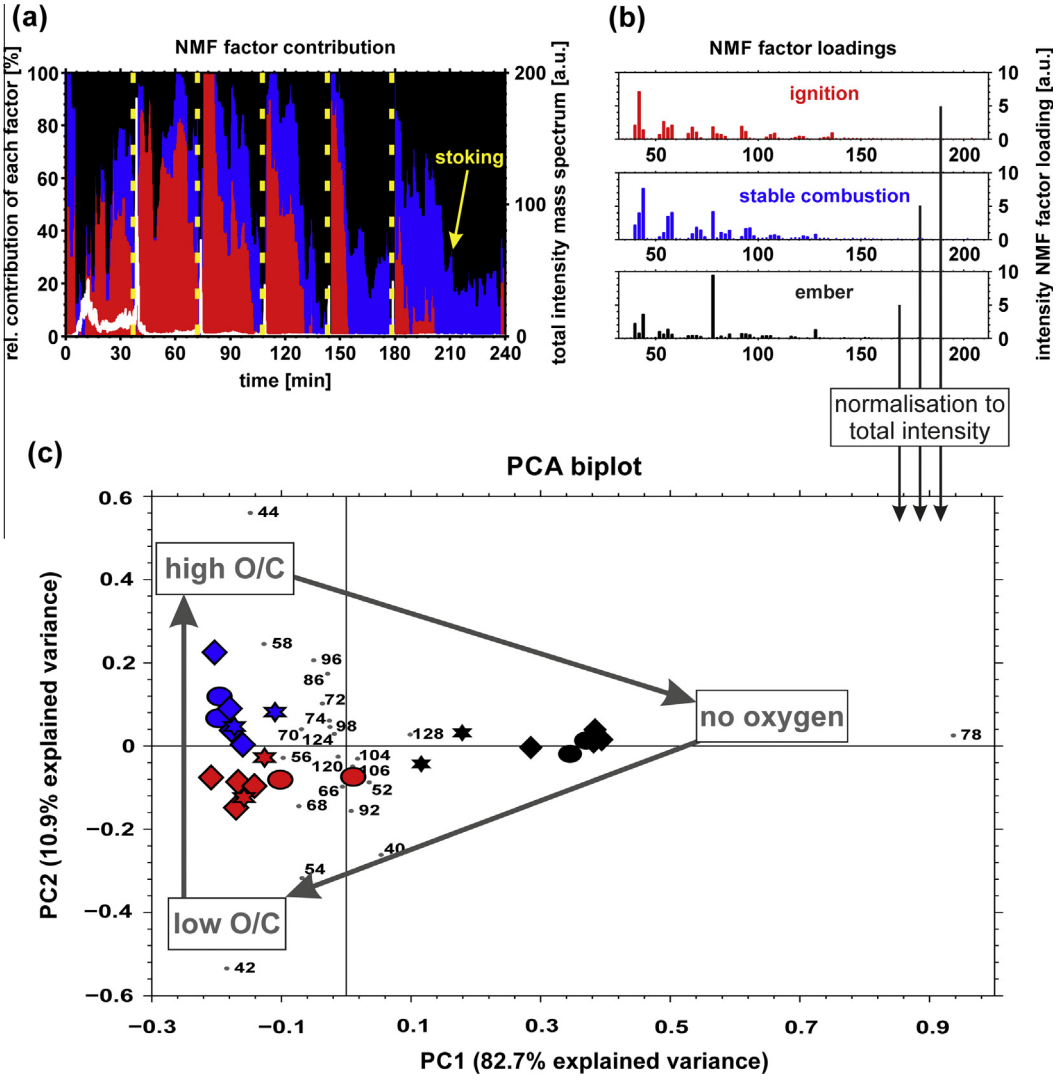

Fig. 3. (a) Relative NMF factor contribution representing burning phases 'ignition', 'stable combustion' and 'ember' and total intensity of original mass spectra (white). Batch limits are indicated by yellow dashed lines. (b) NMF factor loadings which can regarded as mass spectrum for the respective burning phase. (c) PCA-biplot of the first two principal components (PC1 and PC1) for NMF factor loadings of 'ignition' (red), 'stable combustion' (blue) and 'ember' (black). Score coefficients for types of wood are marked with circles (beech), diamonds (birch) and hexagrams (spruce). Grey diamonds with numbers refer to m/z in PC loadings, which can be classified according to their estimated oxygen-to-carbon ratio O/C. For a better visualisation, only factor loadings >0.015 in at least one PC are illustrated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cyclopentadiene (m/z 66), vinylacetylene (m/z 52), C_2-benzene (m/z 106), styrene (m/z 104) and indane (m/z 118). Because of nominal mass resolution, m/z 68 and m/z 106 can also be allocated to furan and benzaldehyde. In contrast to positive PC2 loadings, these m/z do not constitute wood-specific combustion products and are most likely formed by secondary reactions such as water dissociation from hydroxyl groups through chemical elimination reactions or pyrosynthesis in flames. Therefore, even though generally highest emissions occur during the ignition of new logs, the ratio of primary to secondary decomposition products is lower for the burning phase 'ignition' compared to 'stable combustion'. When the wood combustion turns through the formation of char into glowing embers, benzene formed by pyrosynthesis is the most prominent VOC by far.

Estimating the oxygen-to-carbon ratio O/C of detected m/z, the combustion progress might be monitored on-the-fly by SPI-TOFMS. All together, starting from 'ember' in the PCA score plot, burning phases are distributed clockwise towards an increasing O/C ratio and higher proportion of primary decomposition products on the organic emission.

4. Conclusion

This study investigated VOC to SVOC emissions from log wood combustion in a commercially available modern masonry heater burning three commonly types of firewood (beech, birch and spruce). Special focus was placed on the temporal trend of VOC and IVOC during the combustion process using the benefits of SPI-TOFMS. Some hazardous VOC, such as butadiene or styrene, could be semi-quantified. Updated emission factors (EF) for state-of-the-art wood stoves are important to feed atmospheric models for calculations of emission inventories and prediction of future scenarios. If air staging becomes more established in the future, the local atmosphere of areas with much residential wood combustion will change, so atmospheric metrics such as the ratio of toluene to benzene would have to be reconsidered.

Combustion conditions play a more important role for the emissions: Especially the ignition of the first batch is crucial, which has been demonstrated by a detailed comparison of the experiments 'spruce1' and 'spruce2'. Organic emissions increase dramatically if the temperature drops during the ignition before the stable burn-

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ing phase has been reached. In particular, primary decomposition products from lignin or carbohydrates were more enhanced than unsaturated hydrocarbons from secondary decomposition and pyrosynthesis. In general, intensities of all m/z in the first two batches represented more than 50% of the total intensity of the respective m/z from six consecutive batches; even 55–66% of benzene in the exhaust gas was released during the first batch solely. This shows that the development needs regarding the organic emissions from modern masonry heaters are particularly in controlling combustion efficiency during ignition and in the first wood batches.

Additionally, the molecular signature of burning phases was determined by non-negative matrix factorisation (NMF) and more detailed examined by principal component analysis (PCA). This enables to monitor burning phases on-the-fly by the ratio of primary decomposition products from lignin and (hemi-)cellulose to secondary decomposition or pyrosynthetic products for a better understanding of the wood combustion process.

Compared to previous studies with masonry heaters without air staging, the amount of organic emissions dropped significantly. However, toxicological studies must follow, for example by exposure of wood combustion aerosol to lung cells in an air-liquid-interface (ALI) [45,46] to reveal synergistic effects and enable a full assessment of improvements in stove construction.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

This work was carried out at the University of Eastern Finland, Department of Environmental Science in cooperation with Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE), funded by The Helmholtz Impulse and networking Funds of the Helmholtz Association (Germany, HICE), the Academy of Finland (grants 259946 and 258315) and the University of Eastern Finland for the project "sustainable bioenergy, climate change and health". Furthermore, the authors would like to acknowledge Dr. Martin Sklorz and Christopher P. Rüger for their suggestions and critical comments.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.fuel.2016.03.036.

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