2017

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Elsevier BV

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http://dx.doi.org/10.1016/j.atmosenv.2017.03.040

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PII: S1352-2310(17)30172-3
DOI: 10.1016/j.atmosenv.2017.03.040
Reference: AEA 15251

To appear in: Atmospheric Environment

Received Date: 2 September 2016
Revised Date: 14 March 2017
Accepted Date: 21 March 2017


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Time-resolved Analysis of Primary Volatile Emissions and Secondary Aerosol Formation Potential from a Small-Scale Pellet Boiler

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Keywords: VOC, photoionization, SP-AMS, PAM flow reactor, wood combustion, SOA
Abstract
Small-scale pellet boilers and stoves became popular as a wood combustion appliance for domestic heating in Europe, North America and Asia due to economic and environmental aspects. Therefore, an increasing contribution of pellet boilers to air pollution is expected despite their general high combustion efficiency. As emissions of primary organic aerosol (POA) and permanent gases of pellet boilers are well investigated, the scope of this study was to investigate the volatile organic emissions and the formation potential of secondary aerosols for this type of appliance. Fresh and aged emissions were analysed by a soot-particle aerosol time-of-flight mass spectrometry (SP-AMS) and the molecular composition of the volatile precursors with single-photon ionisation time-of-flight mass spectrometry (SPI-TOFMS) at different pellet boiler operation conditions. Organic emissions in the gas phase were dominated by unsaturated hydrocarbons while wood-specific VOCs, e.g. phenolic species or substituted furans, were only detected during the starting phase. Furthermore, organic emissions in the gas phase were found to be correlated to fuel grade and combustion technology in terms of secondary air supply. Secondary organic aerosols of optimised pellet boiler conditions (OPT, state-of-the-art combustion appliance) and reduced secondary air supply (RSA, used as a proxy for pellet boilers of older type) were studied by simulating atmospheric ageing in a Potential Aerosol Mass (PAM) flow reactor. Different increases in OA mass (55 % for OPT, 102 % for RSA), associated with higher average carbon oxidation state and O:C, could be observed in a PAM chamber experiment. Finally, it was found that derived SOA yields and emission factors were distinctly lower than reported for log wood stoves.
1. Introduction

Since the mid-nineties, the demand in Europe for wood pellets as a fuel for domestic heating grows steadily due to high fossil fuel prices, fuel taxes, incentives for renewable energy and CO₂-balance (Cocchi, 2011; Madlener and Koller, 2007). In 2010, the pellet consumption in the European Union (EU27) accounted for 9.8 mio tons (Audigane et al., 2012) while an expanding market is expected for Europe, North America and Asia (Cocchi, 2011). Wood pellets can be utilised in stoves or boilers, whereby boilers are preferred in Northern and Central Europe. From 2005 to 2010, in Germany as the main European market between 15,000 and 25,000 small-scale boilers (power < 50 kW) were newly installed every year (Audigane et al., 2012). Domestic biomass burning is known to emit large amounts of several air pollutants, such as particulate matter (PM), black carbon (BC), particle-bound organic matter (OM), volatile organic compounds (VOCs), carbon monoxide and NOₓ (Eriksson et al., 2014; Evtyugina et al., 2014; Heringa et al., 2012; Kinsey et al., 2012; Martinsson et al., 2015; Orasche et al., 2012; Stockwell et al., 2014), but in many studies, continuously-fired pellet boilers have been characterised as low-emitting combustion appliances compared to batchwise combustion of wood fuels in modern or conventional log wood stoves (Lamberg et al., 2011a; Obaidullah et al., 2012; Orasche et al., 2012; Ozgen et al., 2014; Reda et al., 2015). However, the raw material for pelletisation and the operating conditions in terms of load have been found to affect the emissions (Chandrasekaran et al., 2013; Heringa et al., 2012; Sippula et al., 2007; Venturini et al., 2015; Verma et al., 2011; Vicente et al., 2015; Win et al., 2012). Additionally, particle emissions from pellet boilers and stoves are considerably higher compared to small-scale oil boilers as an alternative with fossil fuel in single-house heating systems (Kaivosoja et al., 2013).

Emission of organic vapours are often expressed as cumulative quantities, e.g. total hydrocarbons (THC), non-methane hydrocarbons/volatile organic compounds (NMHC/NMVOC) or organic gaseous carbon (OGC), but only few studies have paid attention to the investigation of the molecular composition of VOCs released from pellet boilers (Aurell et al., 2012; Boman et al., 2011; Johansson et al., 2004; Olsson et al., 2003; Sippula et al., 2007).

Among the severe effect on human health by wood combustion aerosol (Jalava et al., 2012; Miljevic et al., 2010; Mülhopt et al., 2016; Sehlstedt et al., 2010), VOC emissions from wood combustion contribute to ambient particle concentrations as secondary organic aerosol (SOA) through gas-to-particle conversion (Hennigan et al., 2011; Heringa et al., 2011; Huang et al., 2015; Keller and Burtscher, 2012). In the atmosphere VOCs are transformed by photolysis, hydroxyl (OH) radicals (typically during daylight hours), nitrate radicals (NO₃) during evening and night-time hours, ozone (O₃), and in coastal and marine areas by chlorine atoms during daylight hours (Atkinson and Arey, 2003).
different effects of human health (Künzi et al., 2013; Nordin et al., 2015) and affect the climate through its higher hygroscopicity and impact on cloud formation compared to the primary organic aerosol (POA) (Trivitayanurak and Adams, 2014). Recently, it has been found that the SOA formation from log wood combustion emissions is strongly dominated only by few compounds (Bruns et al., 2016), which mainly belong to the group of aromatic and functionalised aromatic hydrocarbons. Therefore, high concentrations of VOCs do not have to be related to high SOA formation potential and vice versa. To the best of our knowledge, only few studies have investigated the SOA formation from small-scale pellet stoves, but of the same manufacturer, by using a smog chamber or micro smog chamber flow reactor to generate SOA and a high-resolution aerosol mass spectrometer (Corbin et al., 2015; Heringa et al., 2011; Keller and Burtscher, 2012). In addition to that, the easing effect of pellet boiler emissions on SOA formation from α-pinene was recently described (Kari et al., 2017).

The scope of this study is to give a more detailed view over the organic emissions in the gas phase, to extend the database of emission factors (EFs) of volatile organic compounds (VOC) under different operating conditions for a combustion appliance becoming steadily more common and to evaluate its SOA formation.

2. Experimental

2.1. Combustion appliance and procedure
The combustion experiments were performed with an automatically-fired 25 kW top-feed pellet boiler (PZ25RL, Biotech Energietechnik GmbH, Austria), which is equipped with staged combustion secondary air feed. A detailed description of the combustion appliances can be found elsewhere (Lamberg et al., 2011b). Emissions of the pellet boiler were analysed at different operating conditions including boiler start phase (BSP, n = 7), optimal combustion (OPT, n = 7) and approximately 30 % reduced secondary air supply (RSA, n = 3). Since our combustion appliance is a state-of-the-art pellet boiler, RSA is regarded as a simulation of pellet boiler emissions of previous generations with less optimised combustion technology. The end of BSP was set to the point of time when EF of OGC undercuts the mean EF of OGC for OPT plus three-fold standard deviation. All combustion conditions were carried out with commercially available softwood pellets (Table 1). Additionally, the optimal combustion emissions were investigated with birch bark pellets (BBP, n = 1). In contrast to pellet stoves, which refer to room heating appliances, pellet boilers are usually connected to a reservoir of water for warm water supply, leading to a more continuous operation mode of the boiler rather than start-stop operation.

Table 1
Elemental composition and properties of the wood pellets.

<table>
<thead>
<tr>
<th>unit</th>
<th>LOQ</th>
<th>method</th>
<th>softwood pellets</th>
<th>birch bark pellets</th>
</tr>
</thead>
</table>
2.2. Instrumentation

2.2.1. Gas measurements

Main components of the flue gas including carbon monoxide (CO), carbon dioxide (CO₂), oxygen (O₂) and nitrogen oxides (NOₓ = NO+NO₂) were measured continuously by a gas analyser system (ABB, Limas 11 UV, Switzerland) at 2 s time resolution. The sum emissions of organic gaseous carbon (OGC) were quantified by a flame ionisation detector (ABB, Multi-FID 14, Switzerland), which was calibrated against propane. Water and methane were analysed by Fourier-transformed infrared spectroscopy (FTIR) gas analyser (Gasmet, Finland). All gaseous emissions were measured directly from undiluted stack gas through an insulated and externally heated sampling line at 180 °C.

2.2.2. Single photon ionisation time-of-flight mass spectrometry (SPI-TOFMS) for VOC analysis

VOCs were analysed by a time-of-flight mass spectrometer (TOFMS; Compact Reflectron Time-of-Flight Spectrometer II, Kaesdorf Geräte für Forschung and Industrie, Germany) with single-photon ionisation (SPI) at 118 nm (photon energy of 10.49 eV). A detailed description of the instrumental setup can be found elsewhere (Czech et al., 2016). In brief, undiluted hot flue gas was filtered and sampled at 220°C with stepwise increasing temperature to 245°C to prevent condensation. Entering the ionisation chamber of the mass spectrometer, flue gas components are hit by a laser beam (Nd:YAG, Spitlight400, Innolas GmbH, Germany) with a wavelength of 118 nm for single-photon ionisation (SPI). SPI refers to a soft ionisation technique, thus leading to predominantly molecular ions and low fragmentation. In principle, compounds with ionisation energies below the applied photon energy of 10.49 eV can be ionised (Hanley and Zimmermann, 2009). Finally, mass spectra were acquired at 20 Hz, averaged and stored with 1 s time resolution. During the combustion experiments, D₃-toluene (toluene (methyl-D₃), 98% purity, Cambridge Isotope Laboratories Inc., USA) was constantly added as internal standard (IS) leading to a concentration of 91 µl/m³ (= 91 ppbv) in the raw gas. Semi-quantification of selected volatile species was based on photoionisation cross sections (PICS) relative to the IS of D₃-toluene (Table S1).

2.2.3. Soot-particle aerosol mass spectrometer (SP-AMS)
To analyse the organic fraction of primary and aged pellet boiler OA, a soot particle aerosol mass spectrometer (SP-AMS, Aerodyne Research Inc., USA) (Onasch et al., 2012) was applied with 100% transmission for particles covering a vacuum-aerodynamic diameter from 75 nm to 650 nm (Liu et al., 2007). The SP-AMS is equipped with a continuous wave laser vaporiser at 1,064 nm based on single particle soot photometer technology (SP2, Droplet Measurement Technologies, CO, USA; (Stephens et al., 2003)) which enables in combination with the thermal vaporiser (600 °C) to study non-refractory as well as refractory, light absorbing particles such as refractive black carbon (rBC). Vaporised particle components were ionised by electron impact at 70 eV. Subsequently formed ions were separated in a high resolution time-of-flight mass spectrometer (HR-TOFMS) operated in V-mode from m/z 12 to m/z 555 at a mass resolution of approximately 2,000 at m/z 28. All presented data related to OA were recorded without laser vaporiser. AMS data analysis was performed with the analysis software SQUIRREL v1.55C and the standard HR-ToF-AMS data analysis software Peak Integration by Key Analysis (PIKA v1.16 C) adapted in Igor Pro 6.34 A (Wavemetrics). Determination of HR mass concentrations, elemental analysis and ratio of organic mass (OM) to organic carbon (OC) were performed using standard fragmentation assumptions (Allan et al., 2003; Jimenez et al., 2003), and the methods described by (Canagaratna et al., 2015) and (Aiken et al., 2008), respectively. A detailed description of the instrument performance, data analysis and calibration can be found in (Tiitta et al., 2016).

2.4. PAM flow reactor and ageing experiments

The PAM flow reactor in this study was firstly constructed by (Kang et al., 2007) and basically used in the version and settings described by (Bruns et al., 2015). PAM aims to investigate the maximum OA mass after oxidation of precursor gases, nucleation, condensation and gas-particle-partitioning within a short time period in contrast to real-time ageing in smog chambers. Therefore, elevated concentrations of OH compared to typical ambient levels are applied (Li et al., 2015). Briefly, the PAM comprises of a single glass cylinder of 0.015 m³ (length: 0.46 m, diameter: 0.22 m), equipped with two UV-lamps (peak emission at 185 nm and 254 nm, BHK Inc.). In all ageing experiments, UV-lamps were operated at full power (110 V lamp voltage), generating ozone and OH radicals. Ozone is formed by photolysis of \( \text{O}_2 \) in to \( \text{O}^3\text{P} \) which reacts with \( \text{O}_2 \) and a collision partner. From photolysis of ozone, \( \text{O}^1\text{D} \) is formed and reacts with water to OH radicals (Ehhalt, 1999). To provide appropriate water for this reaction, 1 L min⁻¹ of humidified pure nitrogen (“Nafion humidifier”, Perma Pure LLC) was added to the diluted exhaust (1:20 for both OPT and RSA by a porous tube dilutor) gas before entering the PAM to achieve a relative humidity between 21% and 26%. The sampling flow of 5 L min⁻¹ for measuring instruments and a ring flow of 3 L min⁻¹ result in a residence time of 112.5 s. SPI-TOFMS and SP-AMS sampled without additional dilution from
the PAM except SP-AMS measurements of RSA (additional dilution of 1:10 by ejector dilutor).

The initial concentrations of the ageing experiments with PAM flow reactor are summarised in Table 2. OH exposure to VOCs was determined by the degradation of toluene from the pellet boiler emission (Barmet et al., 2012), analysed by SPI-TOFMS, at a rate constant of \(5.63 \times 10^{-12} \, \text{cm}^3 \, \text{molec}^{-1} \, \text{s}^{-1}\) at 298 K (Atkinson and Arey, 2003). In contrast to (Barmet et al., 2012) who demonstrated their concept on a 2-stroke moped, the pellet boiler emissions feature a distinct lower ratio of VOCs (measured as OGC) to NO\(_x\). Low calculated OH exposures may be a result of partly consumed \(O_3\) in the oxidation of NO to NO\(_2\) and consequently lower OH production rate or reaction of NO\(_2\) with OH to HNO\(_3\) (Tkacik et al., 2014).

One PAM cycle denotes one hour with UV light on and one hour with UV light off while during approximately the first 15 min of one cycle were waited to reach steady-state conditions. For OPT two cycles and for RSA one cycle were included in the data evaluation.

It has been reported that particle wall losses affect the measured SOA yield (Lambe et al., 2011), which accounted for 1% to 33% by mass in previous studies (Bruns et al., 2015; Ortega et al., 2013). It is expected that not more than 30% of the particles are lost based on similar size distributions measured by SP-AMS (Fig. S1) with a transmission of >80% for particles with a mobility diameter >150 nm (Lambe et al., 2011) and a previous study with the same pellet boiler and similar soft wood pellets by Lamberg et al. (2011).

Although it has been recently shown that SOA coating of BC particles affect rBC results from SP-AMS (Ahern et al., 2016), rBC were regarded as stable because of low SOA formation.

Increases in OA mass (OA enhancement ratios (\(ER_{OA}\))) when UV light was switched on were calculated after normalisation to rBC, which intrinsically includes the size-dependence of the particle wall losses in the size-range of AMS particle transmission.

\[
ER_{OA} = \left( \frac{OA_{UV(on)}}{rBC_{UV(on)}} \right) / \left( \frac{OA_{UV(off)}}{rBC_{UV(off)}} \right)
\]

The calculation is equal to the method described by (Grieshop et al., 2009) with replacing BC by rBC. \(ER_{OA} > 1\) stands for a net increase in OA mass where as \(ER_{OA} < 1\) mean a loss in OA mass. Concentrations of OGC inside the PAM were calculated from measurements before the PAM and the respective dilution ratio. In contrast to particles, losses of vapours are regarded as negligible due to the short residence time (Ortega et al., 2013).

An overview of the entire instrumental setup can be found in the supplementary material (Fig. S2).

Table 2
Initial concentrations for PAM flow reactor experiments with optimal pellet boiler settings (OPT) and reduced secondary air (RSA).

<table>
<thead>
<tr>
<th>experiment</th>
<th>POA* (µg m⁻³)</th>
<th>CH₄ (µg m⁻³)</th>
<th>OGC (µg m⁻³)</th>
<th>POA/CO (µg m⁻³ ppm⁻¹)</th>
<th>OH exposureb (10⁶ molec cm⁻³ h)</th>
<th>MCEc</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPT</td>
<td>12</td>
<td>75.6</td>
<td>104</td>
<td>3.8</td>
<td>17.6</td>
<td>0.9993</td>
</tr>
<tr>
<td>RSA</td>
<td>132</td>
<td>10.8</td>
<td>68</td>
<td>17.8</td>
<td>0.9964</td>
<td></td>
</tr>
</tbody>
</table>

*a lower limit due to unknown wall losses, approximately 29-33 % (Bruns et al., 2015)

*b calculated from decay of toluene with UV on and off behind PAM

*c modified combustion efficiency, calculated as Δ[CO₂] / (Δ[CO₂]+Δ[CO])

*d OH exposure not available because of malfunction in data acquisition

3. Results & Discussion

3.1. Primary Emissions

3.1.1. Characterisation of organic vapours in flue gas under different pellet boiler operation conditions

All acquired mass spectra were sorted by operation condition and averaged (Fig. 1). Many of the observed m/z can be assigned to well-known pyrolysis gases from wood combustion, such as propene (m/z 42), acetaldehyde (m/z 44), butane/acrolein (m/z 56), acetone/propanal (m/z 58), benzene (m/z 78) and toluene (m/z 92). In the smaller mass region from m/z 40 to m/z 74, peaks appear in groups (triplets to multiplets) of even m/z over m/z intervals of 6-10. Assuming that the vast majority of the VOC in the emission comprises of carbon, oxygen and hydrogen, the number of possible sum formulae shrinks through meaningful number of double bond equivalents and chemical bonds, which allows postulating sum formulas without information of the exact mass. Peaks of the lowest m/z of those multiplets cannot have a chemically meaningful sum formula containing oxygen. Therefore, the mass spectra give evidence that polyunsaturated hydrocarbons, such as propadiene/propyne (m/z 40), vinylacetylene (m/z 52) or cyclopentadiene (m/z 66) are over-proportionately represented in pellet boiler emissions compared to less controlled wood combustion (Czech et al., 2016). The upper m/z of the multiplets likely appertain to carbonyl compounds, indicating a general low abundance of volatile oxygenates in the pellet boiler emission. Phenolic species from lignin (guaiacol m/z 124, methyl-guaiacol m/z 138, vanillin m/z 152) and furans from carbohydrate degradation (methyl-furan m/z 82, furfural m/z 96, furfuryl alcohol m/z 98) emerge with higher abundances from the BSP mass spectrum compared to other operation conditions. Thus primary decomposition of the wood biopolymers plays only an important role in the combustion during the starting phase of the boiler, where the highest abundances for any m/z could be observed, despite the higher PICS and associated sensitivity of SPI for aromatic species (Adam and Zimmermann, 2007).

When the boiler operates with optimal conditions OPT, most m/z > 100 Th observed in BSP drop below the limit of detection. When the secondary air supply was reduced by 30 %, intensities of aromatic hydrocarbons, such as benzene (m/z 78) and naphthalene (m/z 128),
increased by one order of magnitude, whereas aliphatic polyunsaturated hydrocarbons, such as vinylacetylene (m/z 52) and butadiene (m/ 54), increased by 50% and 300%, respectively. However, oxygenates, such as acetaldehyde (m/z 44) and C3-carbonyls (m/z 58) remained constant compared to OPT. Hence, the RSA combustion scenario leads to the highest ratio of unspecified to biomass-related products of incomplete combustion, which may aggravates the assignment of pellet boiler emissions to wood combustion in source apportionment studies. The burning of low-grade wood pellets produced from birch bark results in comparable quantitative VOC emissions to RSA with high-quality softwood pellets regardless the optimal combustion conditions. Higher emissions of aromatics hydrocarbons compared to OPT (e.g. benzene, toluene, naphthalene) can be explained by the higher content of lignin (Krutul et al., 2011) and consequently higher content of aromatic (phenolic) species in the bark compared to the stem.

3.1.2. Modified combustion efficiency, concentrations and emission factors of gases and VOCs

Mean EFs in mg/MJ with standard deviation for repeated measurements were calculated according to the Finnish Standard Association method SFS 5624 as described by (Reda et al., 2015) and presented in Table 3. Additionally, median, 5th and 95th percentile of all data points under one condition can be found in Table S2 of the supplemental material, which describes the temporal appearing variances of the emission in a more appropriate manner. The observed modified combustion efficiencies (MCE = ΔCO2/((ΔCO2+ΔCO)) were found to be generally high (>0.99) for all continuous operations OPT, RSA and BBP at full load, which emphasises the very efficient combustion. Analyte time traces of an experimental run covering all four operating conditions are illustrated in Fig. 2 to underline different types of temporal evolutions.

From BSP to OPT, CO2 increased to (8.6±0.3)% and O2 decayed to (11.9±0.3)% from ambient levels. EF of NOx were found to have almost equal means in BSP and OPT, but different standard deviations (BSP: (63.8±7.4) mg/MJ); OPT: (63.5±2.9) mg/MJ). The reduced secondary air and associated reduced oxygen supply slightly declined NOx-EF to (57.7±1.1) mg/MJ, whereas the birch bark pellet combustion under optimised conditions increased NOx to 131.0 mg/MJ. Compared to softwood pellets birch bark pellets contain twice as much nitrogen (Table 1), indicating that NOx emissions are mainly caused by fuel-nitrogen oxidation (Garcia-Maraver et al., 2014).

The progression of CO-EF was similar to EF of OGC: Both EFs peaked during BSP with mean EFs of (580.0±270.4) mg/MJ (CO) and (55.0±28.9) mg/MJ (OGC), but decreased rapidly to less than 1% of the maximum EF within 2 min after start. During OPT, the pellet boiler emits very low amounts of OGC ((1.3±0.1) mg/MJ) and CO ((45.9±9.0) mg/MJ), respectively. Waiving full secondary air supply was found to increase CO
(382.3±93.8 mg/MJ) by almost one order of magnitude and OGC (2.9±0.6 mg/MJ) by a factor of two compared to OPT, which emphasises the benefit of this advanced combustion technology. Switching to low-grade birch bark pellets leads to a similar effect in terms of OGC (3.4 mg/MJ) and CO (180.9 mg/MJ).

Although both low-grade BBP and RSA enhance OGC-EF, increased levels of single organic vapours turned out differently. Compared to OPT, OGC increased at RSA by 120 %, but acetaldehyde as a representative for oxygenates remained almost constant, whereas the polyenes vinylacetylene and butadiene rose by 100 % and benzene even by one order of magnitude. For BBP, higher releases could be observed for benzene, toluene and styrene, which might be enhanced by the higher availability of substituted aromatics from higher lignin content of the birch bark pellets (Krutul et al., 2011) and formation through cracking of side chains, but also for butadiene.

Classing the applied pellet boiler with small-scale automatically-fed pellet boiler of previous studies, it can be summarised that emission factors of CO and volatile organics were at the lower end of the published range, whereas NOx was located in the mid-range of literature EFs (Table S3), which is mainly caused by the lower nitrogen content of the pellets. Low ratios of VOCs to NOx are regarded as an indicator for a low potential secondary aerosol formation by OH (Ervens et al., 2008). Under optimal operation the ratio of OGC to NOx does not exceed 0.05 unless the secondary air is reduced which can temporarily increase OGC/NOx up to a still low value of 1.5.

Table 3

Modified combustion efficiency, mean concentrations of O2 and CO2 (both in %) and EFs for organic gaseous carbon (OGC), CO, NOx and selected VOCs (in mg/MJ) at four operating conditions.

| MCE | O2 | CO2 | CO | NOx | OGC | PRP m/z 42 | AA m/z 44 | VA m/z 52 | BTD m/z 54 | BENZ m/z 78 | TOL m/z 92 | STYR m/z 104 | IND m/z 116 | NAP m/z 128 | MNAP m/z 142 |
|-----|----|-----|----|-----|-----|-----------|----------|---------|----------|-------------|----------|------------|--------|----------|---------|---------|
|    | 0.9008 | 14.64 | 5.98 | 580.02 | 63.78 | 55.03 | 6.284 | 18.933 | 1.396 | 2.255 | 3.434 | 0.836 | 0.283 | 0.137 | 0.297 | 0.047 |
|    | 0.9993 | 11.93 | 8.57 | 45.92 | 63.49 | 1.30 | 0.037 | 0.238 | 0.011 | 0.016 | 0.023 | 0.007 | 0.004 | 0.002 | 0.010 | 0.005 |
|    | 0.9928 | 11.73 | 8.62 | 382.27 | 57.74 | 2.91 | 0.055 | 0.297 | 0.035 | 0.031 | 0.215 | 0.018 | 0.011 | 0.005 | 0.070 | 0.009 |
|    | 0.9969 | 11.89 | 7.85 | 180.93 | 131.60 | 3.44 | 0.102 | 0.291 | 0.029 | 0.071 | 0.151 | 0.020 | 0.010 | 0.003 | 0.035 | 0.005 |

PRP – propene; AA – acetaldehyde; VA – vinylacetylene; BTD – butadiene; BENZ – benzene; TOL – toluene; STYR – styrene; IND – indene; NAP – napthalene; MNAP – methylnaphthalene; EFs can be converted into mg/kg wood by using lower heating values of softwood and birch bark pellets from Table 1.

3.2. Secondary formation potential from PAM flow reactor

Pellet boiler emission for OPT and RSA passed through the PAM with UV-lights switched on and off. Data points at steady-state conditions were examined for statistically significant differences of their arithmetic means by two-sample Student’s t-test.

3.2.1. Secondary VOC species
Apart from carbonyls, intensities of all volatile species declined regardless the combustion condition. For OPT conditions the homologue series of C$_2$- to C$_5$-carbonyls (m/z 44 to m/z 86) increased significantly ($p < 1 \times 10^{-6}$) by a factor of six for acetaldehyde and a factor of two for C$_3$- to C$_5$-carbonyls compared to the primary emission (Fig. S3). Further secondary volatile species could not be detected by SPI-TOFMS due to too high ionisation energies, possible fragmentation or too low concentrations. A statement about the secondary volatile species for RSA cannot be made because of a malfunction in data acquisition.

### 3.2.2. OA enhancement ratios ER$_{OA}$

Oxidation and enhanced functionalisation of volatile precursors result in decreasing vapour pressures leading to condensation, secondary particle formation and SOA. OA can also increase by heterogeneous oxidation of particulate organic matter (aged POA) (Browne et al., 2015). Based on the available data, it cannot be differentiated between aged POA and SOA. However, it was found that heterogeneous reactions of OH do not play a significant role at observed low OH exposures (Cappa and Wilson, 2012).

OA gained 1.55-fold additional mass (ER$_{OA}$, $p = 0.162$) after photooxidation of pellet boiler emission under stable OPT conditions. Only Keller & Burtscher (2012) observed SOA formation for the stable burning condition of a pellet stove with a micro-smog chamber (MSC), whereas no SOA was observed by Corbin et al. (2015) with the same ageing apparatus. With a smog chamber (SC) SOA yields were only observed for the pellet burner starting phase which emits higher amounts of VOCs than the stable burning phase for which SOA formation appeared within the uncertainty of wall loss correction (Heringa et al., 2011). Two possible explanations can be given by the different types of ageing reactor and combustion appliances: The MSC features shorter residence times, which can favour photo-fragmentation reaction and avoid particle coagulation (Bruns et al., 2015), leading to lower increases of OA and explaining the absence of SOA in the experiment of Corbin et al. (2015). Furthermore, the different type of combustion appliances likely play the major role for explaining the different SOA formation between Keller & Burtscher (2012) and Corbin et al. (2015) as well as between this study and Heringa et al. (2011) because it has been shown that PAM and SC generate comparable increases of OA exposing POA to the same total level of OH (Bruns et al., 2015). The gained relative weight in OM may suggest distinct SOA formation, but the initial POA concentration was low compared to organic compounds in the gas phase (Table 2), which might be the reason for the insignificance of OA increase.

Despite low concentrations of OGC during OPT, many (poly)unsaturated aliphatic hydrocarbons were detected in the primary emission which generally exhibit a high reactivity under OH and O$_3$ towards formation of highly functionalised SOA compounds (Ng et al., 2006). Due to the decreased vapour pressure even highly functionalised SOA components with a relatively low carbon number can condense on particles or form condensation nuclei.
On that account, it is likely that the high number of double bond equivalents of the primary emitted organic compounds induce higher gas-to-particle conversion rates than other organic vapours of lower double bond equivalent numbers.

Photooxidation of RSA pellet boiler emissions led to a higher growth in OA than photooxidation of OPT emissions with an ER$_{OA}$ of 2.02 ($p = 2.8 \cdot 10^{-4}$). The reduction of secondary air by 30% enhances POA mass by a factor of $\sim 5$, which agrees with the findings of (Lamberg et al., 2011b), whereas OGC in this study increased only by a factor of $\sim 1.5$ (Table 3). Similar to the higher ER$_{OA}$, RSA revealed higher SOA formation on an absolute scale, where the increase in OA is even one order of magnitude higher for RSA than OPT. It might be that the relatively low OH exposure of $17.6 \cdot 10^6$ molec cm$^{-3}$ h did not cover the full SOA formation potential. Towards higher relative humidity as used in other ageing studies of wood combustion emissions, the OH concentration were found to increase exponentially (Bruns et al., 2015), thus the observed ER$_{OA}$ and related quantities represent lower limits.

3.2.3. Elemental ratios, average carbon oxidation state (OSC) and OM/OC

Under both operation conditions OPT and RSA, POA covered similar O:C of $1.07 \pm 0.41$ (OPT) and $1.12 \pm 0.24$ (RSA), which increased to $1.78 \pm 0.09$ (OPT) and $1.37 \pm 0.24$ (RSA) after photooxidation. Both O:C for POA and aged OA are higher than previously reported ratio 0.23 and 0.5 for stable burning (Heringa et al., 2011), but for POA a wide range of O:C for different pellet boiler makes up to 1.59 can be found for a 15 kW pellet boiler during stable combustion (Heringa et al., 2012). One reason for higher O:C compared to previous studies lies in the application of improved elemental analysis of AMS data which may enhance calculated O:C by 27% related to the previous algorithm (Canagaratna et al., 2015). Additionally, high amounts of carbonates were found in pellet boiler particulate emissions (Lamberg et al., 2011a), which also might contribute to the CO$_2$ signal in the AMS spectra and enhance O:C (Bozetti et al., 2017). Nevertheless the increase of O:C is not affected since it is not known that photooxidation has an direct impact on the carbonate content. Recently, it has been demonstrated that KNO$_3$ have a positive bias on the CO$_2$ signal through reaction on the vaporiser and consequently increases O:C as well (Pieber et al., 2016). However, the impact of KNO$_3$ cannot be estimated because the AMS do not give quantitative data on potassium which inhibits the unambiguous assignment of NO$_3$ to NH$_4$NO$_3$, organic nitrates and KNO$_3$. The ratio H:C behaved inversely to O:C and declined from $1.21 \pm 0.2$ (OPT) and $1.31 \pm 0.15$ (RSA) to $0.88 \pm 0.05$ (OPT) and $1.20 \pm 0.15$ (RSA). The relatively high degree of scattering for non-aged POA of OPT may be a consequence of low concentrations which implies higher errors for elemental analysis. Similar to previous studies (Corbin et al., 2015; Heringa et al., 2011), both POA and aged OA is located outside the triangular space where usually ambient aerosols can be found (Ng et al., 2010), which is possibly caused by faster gas-phase oxidation relative to particle nucleation (Lambe et al.,
The average carbon oxidation state (OSC) (Kroll et al., 2011) increased accordingly to 
O:C from 0.88±0.94 (OPT) and 0.93±0.55 (RSA) to 2.68±0.23 (OPT) and 1.55±0.6 (RSA) 
(Fig. 3).

Taking into consideration that apart from carbonyls all m/z appeared with lower abundances 
in the SPI mass spectra with UV-lights on, gas-to-particle conversion was more likely the 
main mechanism for increasing OA mass than heterogeneous oxidation. The OM/OC ratios 
were elevated from 2.39±0.78 (OPT) and 2.60±0.31 (RSA) to 3.44±0.12 (OPT) and 2.93±0.31 (RSA). Moreover, the slope of H:C vs. O:C of aged OA provides information about 
oxidation mechanisms. Slopes of -0.44±0.07 (OPT) and -0.47±0.10 (RSA) were slightly 
higher than for aged wood burning aerosol (Ortega et al., 2013), but revealed that the 
addition of carboxylic groups associated with C-C bond breakage was the dominating 
mechanism (Ng et al., 2011) (Table S4).

### 3.2.4. High resolution mass spectrometric analysis of pellet boiler PM

The high resolution of the SP-AMS enables separation of isobaric ions and subsequent 
sorting into classes. Oxygenated species CHO\(_1\) and CHO\(_{n>1}\) dominated mass spectra of POA 
with 11 % and 53 % while CH represented 6 % in particles of OPT. For RSA, POA contained 
similarly high fractions of CHO\(_{n>1}\) (47 %) and more of CH (22 %) and CHO (18 %) compared 
to OPT. CH species decayed during ageing covered by increasing fractions of oxygen- and 
nitrogen-containing species as expected. However, while CHO\(_{n>1}\) (for OPT and RSA) and 
CHO (for OPT) remained almost constant during ageing, aged OA from RSA emissions 
contained a significantly larger fraction of single-oxidised species CHO than non-aged POA 
(Fig. 4). Furthermore, the remaining organic fraction (total organic reduced by CH, CHO and 
CHO\(_{n>1}\)) of most likely CHN and CHNO species (= CHN(O)) were elevated from 4 % to 13 % 
for RSA and from 26 % to 29 % for OPT, indicating the formation of nitrogen-containing 
organic compounds such as peroxyacetyl nitrates or nitro compounds.

In a detailed view at single ions (Fig. S4), significant increases for RSA of not less than 
100 % were observed for C\(_2\)H\(_3\)O\(^+\) (m/z 43), CO\(_2\)\(^+\) (m/z 44) and C\(_2\)H\(_4\)O\(_2\)\(^+\) (m/z 60) which 
belong to typical SOA compound classes of non-acid oxygenates, carboxylic acids and long-
chain carboxylic acids (Ng et al., 2011). In particular, the fragment C\(_2\)H\(_4\)O\(_2\)\(^+\) (m/z 60) has 
been extensively discussed in the literature due to its application as marker for biomass 
burning, but also contributions from both SOA components and anhydrous sugars, such as 
levoglucosan, mannosan and galactosan (Elsasser et al., 2012; Heringa et al., 2011). The 
pure hydrocarbon fragments C\(_3\)H\(_7\)\(^+\) (m/z 43) and C\(_4\)H\(_9\)\(^+\) (m/z 57) decreased by 34 % and 
44 % for RSA, respectively. Interestingly, the aromatic-related fragment C\(_6\)H\(_5\)\(^+\) (m/z 77) 
significantly declined by 43 % (p = 0.020) for RSA, but increased by 77 % for OPT albeit 
insignificantly (p = 0.084). Taking the higher ratio of VOCs to POA for OPT into 
consideration, a transfer of oxygenated aromatics from the gaseous phase to the particulate
phase could have caused increasing $\text{C}_6\text{H}_5^+$ fragments. During ageing aromatic rings can only be retained by oxidation of side chains of substituted single-ring aromatics or PAHs. For example, the oxidation of toluene or naphthalene yields in benzaldehyde and phthalic acid, respectively (Riva et al., 2015; Wu et al., 2014). As opposed to RSA, OPT did not reveal any significant ($p < 0.05$) increase for any fragment ion except $\text{C}_2\text{H}_3\text{O}^+$ (m/z 43) by 510% ($p = 6.16 \cdot 10^{-4}$) (Table S5).

### 3.2.5. Secondary organic carbon bulk yield ($\text{SOC}_{\text{yield}}$) and SOA formation potential

To calculate bulk yield of secondary organic carbon ($\text{SOC}_{\text{yield}}$), non-aged POA concentration was subtracted from aged OA concentration to obtain SOA resulting from gas-to-particle conversion. The known ratio of OM to OC was further incorporated to calculate the concentration of secondary SOC. Finally, SOC was set in relation to OGC, reduced by methane to non-methane organic gaseous carbon (NMOGC) (Table 2), assuming an equal FID response factor for both propane and methane, to reveal the relative amount of OGC which was transferred from gaseous into the particulate phase. For the SOC yield we assume that all NMOGC reacted despite the for PAM chamber relatively low OH exposure.

$$\text{SOC}_{\text{yield}} = \frac{(\text{OA}_{\text{aged}} - \text{POA})}{((\text{OM}/\text{OC})_{\text{aged}} \cdot \text{NMOGC})} \cdot 100\% \quad (2)$$

While for RSA the conversion from OGC to SOC was 39.5%, for OPT 4.1% of NMOGC reacted with atmospheric oxidising agents to products of lower volatility which condense in the particulate phase. Thus, modern small-scale pellet boilers do not only emit low amounts of OA, but also account for a low contribution to the total particle level in ambient air after atmospheric conversion processes.

An estimation of SOA formation potential for BSP and BBP can be done by consideration of most contributing species to SOA formation (indicated by asterisk). Multiplication of $i$ EFs of primarily emitted species, in this case of benzene, toluene, indene, naphthalene and methyl-naphthalene (Table 3), with their respective SOA yields (Bruns et al., 2016)

$$\text{SOA}^*-\text{EF} = \sum \text{EF}_i \cdot \text{SOA}_{\text{yield},i} \quad (3)$$

leads to SOA* potentials of 1661 µg/MJ (BSP), 17 µg/MJ (OPT), 108 µg/MJ (RSA) and 80 µg/MJ (BBP). Similar to (Heringa et al., 2011) the start phase BSP was found to emit higher levels of SOA precursors than the stable combustion phase OPT. However, $\text{ER}_{\text{OA}^*}$ of all combustion conditions appear in the small window of 1.33 to 1.36 and are lower than the obtained $\text{ER}_{\text{OA}}$ from PAM experiments. The six considered organic species represent only a snapshot of organic vapours with significant SOA formation potential. Comparing SOA-EFs and SOA* -EFs, the consideration of the six precursor leads only to one third of observed SOA formation from PAM experiments for OPT, while for RSA SOA-EFs is even one order of magnitude higher than SOA* indicating that distinctly more than the six considered precursors have a significant impact on SOA formation. In particular, oxygenated
monoaromatics, including phenol, methoxy-phenol or benzaldehyde, feature high SOA yields and may contribute significantly even at low concentrations. Moreover, some components e.g.acenaphthylene (m/z 152) or phenylacetylene (m/z 102), may contribute to the same extent as styrene to SOA formation (Bruns et al., 2016), but could not be quantified and thus may account for the observed discrepancy. The SOA obtained by the combustion of the same amount of wood differs by one order of magnitude for this study compared to Keller & Burtscher (2012) for optimal as well as for reduced air conditions (Table 4), but their pellet stove was not equipped with air staged secondary air supply. Furthermore, both observed and calculated SOA mass per MJ during OPT are two orders of magnitude below the mean EF of 5±5.5 mg/MJ reported for the flaming phase of modern log wood stoves and three orders of magnitude lower than old wood stoves (Heringa et al., 2011). However, it should be kept in mind that EFs for batchwise log wood combustion and consequently the SOA formation potential, which is often reported solely for the first batch, may change enormously with ongoing batches when the temperature of the stove’s combustion zone increases (Czech et al., 2016). Nevertheless, regarding these four combustion appliances, it is concluded that with improved combustion conditions not only the emission of VOCs is reduced, but also the SOA formation is suppressed.

**Table 4**

Emission factors of SOA from PAM experiments, (*) derived from sum of SOA yields of single precursors and literature data in mg/MJ with standard deviation in brackets

<table>
<thead>
<tr>
<th>combustion condition</th>
<th>This study</th>
<th>This study*</th>
<th>Heringa et al. 2011*</th>
<th>Keller &amp; Burtscher 2012b</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSP</td>
<td>1.661</td>
<td>28.5</td>
<td>(1.811)</td>
<td>(11.4)</td>
</tr>
<tr>
<td>OPT</td>
<td>0.053</td>
<td>0.017</td>
<td>(0.004)</td>
<td>0.394 (0.092)</td>
</tr>
<tr>
<td>RSA</td>
<td>1.150</td>
<td>12.22 (0.39); 51.46 (0.37); 325.83 (6.19)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BBP</td>
<td>0.080</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*based on SOA yields at OH exposures from 45 to $95 \times 10^6$ molec cm$^{-3}$ h of benzene, toluene, styrene, indene, naphthalene and methyl-naphthalenes (Bruns et al., 2016) with an uncertainty of ±50 %; propagation error in brackets

*converted from g/kg assuming a lower heating value of 20 MJ/kg

*converted from mg/kg-CO$_2$ assuming carbon content of 0.5 and lower heating value of 20 MJ/kg, three different settings of reduced air supply

**4. Conclusion**

Primary and aged organic aerosol as well as VOCs from a small-scale pellet boiler were investigated by SP-HR-AMS and SPI-TOFMS. During continuous operation OPT, RSA and BBP, the pellet boiler emits one order of magnitude less VOCs, which mainly belong to the class of (poly)unsaturated hydrocarbons, compared to modern masonry heated burning logwood. Only in BSP and to a lower extend in BBP, typical wood combustion-related VOCs from the decomposition of carbohydrates and lignin, such as substituted furans and phenols, could be detected, which might bias apportionment to emission sources from measurements of ambient air.
In experiments with the PAM flow reactor, ER\textsubscript{OA} of 1.55 and 2.02 were found for aged OA of OPT and RSA, respectively, which emphasises the relevance of organic vapours to total OA emission in ambient air not only for log wood stoves, but also for pellet boilers. Furthermore, the SOA formation potential was found to decrease with improvements of combustion technology from old log wood stoves (Heringa et al., 2011) to pellet boilers with air-staged secondary air supply by three orders of magnitude. However, a higher number of replicates has to support the evidence from these ageing experiments.

The fragment C\textsubscript{2}H\textsubscript{4}O\textsubscript{2}\textsuperscript{+} (m/z 60) represents the contribution of anhydrous sugars, mainly levoglucosan, to the mass spectrum of POA. In agreement with the findings of Heringa et al. (2011), a growth for this fragment was observed after ageing which expresses the contribution of pellet boiler SOA to the overestimation of primary biomass combustion emission in source apportionment studies derived from this fragment.

Altogether, our results demonstrate that VOC emissions from pellet boilers, as a growing combustion technology for domestic heating, cannot be regarded as typical wood combustion emission. Low emissions of VOCs are connected with low secondary aerosol formation potential compared to modern log wood stoves, which emphasises the role of pellet boilers as clean wood combustion appliances. Finally, this investigation also motivates to look closer into the change of the chemical composition of fresh aged particles from wood pellet combustion which is important in context with potential health effects associated with primary and aged emissions.

Acknowledgement

The measurements were carried out at the University of Eastern Finland (UEF), Department of Environmental and Biological Science, in cooperation with the Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health (HICE), funded by The Helmholtz Impulse and networking Funds of the Helmholtz Association (Germany), the DACH-project WooShi (grant ZI 764/5-1), the Academy of Finland (grants 259946, 258315 and 304459) and the University of Eastern Finland for the project “sustainable bioenergy, climate change and health”. Furthermore, Felix Klein is gratefully acknowledged for his valuable comments on the calculations.

References


biomass-burning soot by two particle mass spectrometers. Atmospheric Measurement Techniques 9, 6117-6137.


particulate emissions from residential biomass heating systems based on old and new technologies.

Atmospheric Environment 50, 24-35.


Pieber, S.M., El Haddad, I., Slowik, J.G., Canagaratna, M.R., Jayne, J.T., Platt, S.M., Bozzetti, C.,
Daellenbach, K.R., Fröhlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jiménez, J.L., Worsnop,
and ACSM Organic Aerosol Composition Studies. Environmental Science and Technology 50, 10494-
10503.
Reda, A.A., Czech, H., Schnelle-Kreis, J., Sippula, O., Orasche, J., Weggler, B., Abbaszade, G., Arteaga-
Salas, J.M., Kortelainen, M., Tissari, J., Jokiniemi, J., Streibel, T., Zimmermann, R., 2015. Analysis of
gas phase carbonyl compounds in emissions from modern wood combustion appliances: influence of
wood type and combustion appliance. Energy and Fuels 29, 3897-3907.
Riva, M., Robinson, E.S., Perraudin, E., Donahue, N.M., Villenave, E., 2015. Photochemical aging of
secondary organic aerosols generated from the photooxidation of polycyclic aromatic hydrocarbons
in the gas-phase. Environmental Science and Technology 49, 5407-5416.
Sehlstedt, M., Dove, R., Boman, C., Pagels, J., Swietlicki, E., Löndahl, J., Westerholm, R., Bosson, J.,
airway responses following experimental exposure to wood smoke in man. Particle and Fibre
Toxicology 7.
Sippula, O., Hytönen, K., Tissari, J., Raunemaa, T., Jokiniemi, J., 2007. Effect of wood fuel on the
emissions from a top-feed pellet stove. Energy and Fuels 21, 1151-1160.
Stockwell, C.E., Yokelson, R.J., Kreidenweis, S.M., Robinson, A.L., Demott, P.J., Sullivan, R.C., Reardon,
residue, domestic biofuels, grasses, and other fuels: Configuration and Fourier transform infrared
(FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4). Atmospheric Chemistry
and Physics 14, 9727-9754.
Tiitta, P., Leskinen, A., Hao, L., Yli-Pirilä, P., Kortelainen, M., Grigonyte, J., Tissari, J., Lamberg, H.,
Hartikainen, A., Kuuspalo, K., Kortelainen, A., Virtanen, A., Lehtinen, K.E.J., Komppula, M., Pieber, S.,
Prévôt, A.S.H., Onasch, T.B., Worsnop, D.R., Czech, H., Zimmermann, R., Jokiniemi, J., Sippula, O.,
2016. Transformation of logwood combustion emissions in a smog chamber: formation of secondary
organic aerosol and changes in the primary organic aerosol upon daytime and nighttime aging.
Atmospheric Chemistry and Physics 16, 13251-13269.
Tkacik, D.S., Lambe, A.T., Jathar, S., Li, X., Presto, A.A., Zhao, Y., Blake, D., Meinardi, S., Jayne, J.T.,
emissions using a potential aerosol mass reactor. Environmental Science and Technology 48, 11235-
11242.


Fig. 1. Averaged SPI mass spectra of organic vapours for the four investigated operation conditions of softwood pellets (a) boiler start phase (BSP), (b) optimal combustion (OPT), (c) reduced secondary air supply (RSA) and (d) optimal combustion of birch bark pellets (BBP). The concentration of the internal standard (IS, D₃-toluene) was constant for all experiments and appears with its molecular ion at m/z 95 (bold).
Fig. 2. Temporal evolution of concentrations (O$_2$ and CO$_2$), EFs (NO$_x$, CO, benzene (BENZ), acetaldehyde (AA) and butadiene (BTD)) and modified combustion efficiency over boiler start phase (BSP), optimised combustion (OPT), combustion with reduced secondary air (RSA) of softwood pellets as well as optimised combustion of birch bark pellets (BBP).
Fig. 3. Van Krevelen diagram of aged (red) and non-aged OA (blue) from combustion conditions OPT (circles) and RSA (squares). Solid purple lines belong to slopes from (Heald et al., 2010) which indicate main functionalisation of OA, where the black lines represent slopes from non-aged to aged OA (-0.44±0.07 for OPT and -0.47±0.10 for RSA). The grey area refers to the triangular space of $f_{44}$ vs. $f_{43}$ in which ambient OA was found to be usually located (Ng et al., 2010), converted into the H:C vs. O:C dimension. Dashed lines are average carbon oxidation states (OSC) (Kroll et al., 2011).
Fig. 4. Relative compound class distribution for OPT (circles) and RSA (squares) with standard deviations. Data points below the diagonal line show relative increase in the organic fraction after ageing (ER > 1), whereas data points above the diagonal lines show decrease in relative organic fraction (ER < 1).
Highlights:

- composition of VOC emissions from pellet boiler at different combustion conditions
- very low concentrations of wood-related VOCs in primary emissions
- low primary emissions accompany low secondary SOA formation potential
- total SOA yield measured with PAM and estimated from precursor yields