Response to Referees

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Characterization of gas-phase organics using proton transfer reaction time-of-flight mass spectrometry: fresh and aged residential wood combustion emissions

Emily A. Bruns, Jay G. Slowik, Imad El Haddad, Dogushan Kilic, Felix Klein, Josef Dommen, Brice Temime-Roussel, Nicolas Marchand, Urs Baltensperger and André S. H. Prévôt

We thank the Referees for the comments and we have incorporated the feedback to improve the manuscript. We have copied the remarks of each Referee in *black italics* and our responses are given in regular black font. Manuscript text including revisions is given in *regular blue font*.

Anonymous Referee #1

*Bruns et al. describe controlled laboratory measurements of fresh and aged emissions from the residential combustion of beech wood. The authors generated these emissions using a commercial wood burner. Using a high-resolution proton transfer reaction time-of-flight mass spectrometer, the authors measured primary VOC emissions under stable flaming conditions. For aging experiments, the emissions were directed into a Teflon chamber and oxidized by OH radicals generated from the photolysis of nitrous acid. Primary emissions exhibited significant enhancements of oxygenated species (particularly acids) and aromatic compounds. The emissions of typical nitrogen-containing biomass burning markers, such as acetonitrile, were significantly lower than those observed from open burning. During aging experiments, the authors observed significant consumption of NMOG mass. Certain species, such as formic acid and phthalic anhydride, showed significant enhancements. Acetic acid, however, exhibited no net increase, which the authors attribute to the balancing of secondary production + OH consumption.*

The manuscript is written clearly and the contents are well organized. The study is interesting, well executed, and the results provide insights into the chemical evolution of wood smoke, which is poorly constrained yet important for regional air quality. My primary comments pertain to the conclusions drawn about secondary NMOG and the observations of low acetonitrile. In particular, I believe the authors should provide an expanded discussion (and potentially further insights) into the variability of NMOG oxidation products (see point 2). Upon addressing these comments, I recommend the manuscript for publication.

We have addressed the Referee’s comments as detailed below, including modifying the manuscript to provide an expanded discussion and further insights into the variability of NMOG oxidation products and observations of low acetonitrile emissions.

*Comments*

1) Secondary NMOG:

The authors discuss a number of processes that could affect the observed net decrease in NMOG mass, including gas-to-particle partitioning and conversion of gas-phase species to those that
cannot be detected by the PTR-ToF-MS. However, the authors do not include a discussion about vapor-phase wall loss. Bian et al. (2015) simulated the loss of primary biomass burning emissions to a Teflon chamber and demonstrated that wall loss can significantly affect both particle and gas-phase organics. In the average simulation, ~75% of gas-phase vapors were lost to the chamber. Stockwell et al. (2014) observed losses of biomass burning organic compounds (including acetic acid) to surfaces at very different rates. Can the authors estimate and/or discuss the impact of wall loss and potentially provide uncertainties to the 5 – 30% loss in NMOG mass?

NMOG wall losses were inferred by monitoring NMOG concentrations prior to initiating photochemistry and by assessing the smog chamber conditions affecting loss rates during aging as detailed by Zhang et al. (2014 and 2015) (Zhang, X., Cappa, C.D., Jathar, S.H., McVay, R.C., Ensb erg, J.J., Kleeman, M.J. and Seinfeld, J.H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, Proceedings of the National Academy of Sciences 111, 5802–5807, 2014; Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, Atmos. Chem. Phys., 15, 4197–4214, 2015). Bian et al. (2015) found that the concentration of gas-phase emissions generated during open burning decreased by 86% due to vapor wall losses in a dark chamber using best estimate parameters in a model. When using effective wall saturation concentrations based on the study of Zhang et al., Bian et al. (2015) found that the net vapor loss to the walls decreased by 65% compared to the best estimate. While open biomass burning emission profiles share similarities with residential burning emissions, differences can be large (e.g., see response below regarding emission of nitrogen-containing species), making it difficult to apply the findings of Bian et al. (2015) to residential burning, particularly as vapor losses are very sensitive to the model parameters. We think more investigation of residential wood combustion emissions is needed to be able to apply meaningful uncertainties on the loss in NMOG mass in the current study, but we agree with the Referee that a discussion of potential NMOG wall losses is needed in the manuscript and we have modified the text as follows (Pages 16-17, lines 349-359): “In addition to gas to particle phase partitioning and formation of gas-phase species not quantified here, a decrease in NMOG mass with aging could also be due to losses of gas-phase species to the chamber walls (Zhang et al., 2014; Bian et al., 2015). Measurements of NMOGs in the chamber prior to aging are stable, indicating that the chamber walls are not a sink for NMOGs, but rather that NMOGs are in equilibrium with the chamber walls, particles and the gas phase. Zhang et al. (2014) show that the rate of NMOG wall loss is proportional to seed aerosol concentration and OH concentration, both of which were relatively high in the current experiments (Table S1; OH concentrations were ~1.4x10^7 molec cm^-3). Under these experimental conditions, NMOG wall losses are not expected to be large. However, future studies are needed to provide insight into vapor wall loss of residential wood combustion emissions during aging.”

In addition to wall loss, I think the authors should also discuss the variability of secondary organic production. This discussion is provided for primary emissions (Section 3.2), but few insights are drawn from the variability of oxidation products. There are significant differences between the trends observed during Expts. 2,3 and those observed during Expts. 1,4,5 (Figs. 4 and 5). For example, acids and O-containing compounds show a general increase in Expts 1,4,5, but a decrease in Expts 2,3. It is notable that the initial NMOG distributions in Expts 1,4,5
contain a higher fraction of aromatic and oxygenate aromatics. Could it be that these compounds are a significant source of secondary acids and O-containing compounds? It should also be noted that other compounds not measured by proton-transfer could also impact these trends (e.g. ethylene). This variability is quite interesting and a discussion pertaining to these differences may help in understanding the variability of OVOC formation in open burning (e.g. de Gouw et al. 2006 vs Yokelson et al. 2003).

We agree with the Referee that more discussion on the variability of the aged emission profiles is needed and we have added a new section in the manuscript to address this topic (3.5 Aged emission variability). We have also included the discussion on variability of SOA formation potential in this section. The text has been modified as follows (Pages 19-20, section 3.5): “As described above, the primary emission profiles, as well as total NMOG mass emitted, vary considerably for experiments 2 and 3 compared to experiments 1, 4 and 5, with much higher total NMOG emissions in experiments 2 and 3. It is expected that the aged emission profiles also exhibit variability based on the primary emissions. Total acid and O-containing species decrease with aging in experiments 2 and 3, in contrast to experiments 1, 4 and 5, where these classes increase with aging (Figure 4). Formic acid shows the largest increase with aging in all experiments (~190-480 mg kg\(^{-1}\) relative to the primary EF, Figure 5), however, in experiments 1, 4 and 5, this increase contributes much more to the total acid mass as the total acid mass is ~5-15 times lower compared to experiments 2 and 3. An analogous case occurs for maleic anhydride for the O-containing class of compounds. As formic acid and maleic anhydride are formed from the oxidation of aromatic compounds (Bandow et al., 1985; Sato et al., 2007; Praplan et al., 2014), among others, a higher fraction of aromatic species to the total NMOG emissions will contribute to increases in acid and O-containing NMOGs. Inclusion of NMOGs not quantified by PTR-ToF-MS could impact the trends observed in Figure 4.”

2) Acetonitrile
In Section 3.3, the authors discuss the variability of acetonitrile. The authors attribute the observations of low acetonitrile to burning conditions. While burning efficiency and O\(_2\) fraction certainly affect NMOG emissions, very recent work demonstrates that fuel composition plays a major role in the variability of nitrogen-containing VOCs (Coggon et al. 2016). In that study, the authors show that wood (low nitrogen content) emits a significantly lower fraction of nitrogen-containing VOCs than other tree components, such as leaves and boughs (high nitrogen content).

Given this new work, the authors should also discuss the effects of fuel composition. Assuming that the beech wood is free of stems, twigs, or leaves, then it is likely that low acetonitrile emissions result from the combustion of low nitrogen-containing fuel. Have the authors also considered looking at the emissions of other nitrogen-containing NMOGs that are sensitive to proton-transfer, such as acrylonitrile or HNCO? These species would also likely exhibit lower EFs compared to open burning of fuels with higher nitrogen content.

We thank the Referee for bringing the recent work of Coggon et al. (2016) to our attention. The beech wood in our study was free of stems, twigs, leaves and bark, and based on the work of Coggon et al. (2016), we therefore expect that a relatively low fraction of the total NMOGs was N-containing compared to burning of biomass containing leaves, etc. This fact may explain the relatively low acetonitrile emissions in our study compared to open biomass burning, where
leaves, bark, etc. are typically present. The primary emission factors of C₃H₃N and HNCO ranged in our study from 3.6-6.4 mg kg⁻¹ and BLD (<tens of pptv)-11 mg kg⁻¹, respectively. Emission factors of acrylonitrile (C₃H₃N) observed during open burning are higher than those observed in the current study (~10-90 mg kg⁻¹, Akagi et al., 2013), as expected based on the lower acetonitrile emission factors observed in the current study and the findings of Coggon et al., 2016.

We have expanded the discussion of acetonitrile emissions to include this information (Page 14, lines 288-300): “In agreement with the current study, ambient measurements of acetonitrile made in Colorado (USA) were not associated with fresh residential burning emissions (Coggon et al., 2016). Lower ambient measurements of nitrogen-containing NMOGs (including acetonitrile) during residential burning compared to open burning were attributed to the generally lower nitrogen content in fuels burned residentially (Coggon et al., 2016). Lower nitrogen content of the fuel is likely a contributor to the relatively low acetonitrile emissions in the current study.

The primary emission factors of other nitrogenated species, such as C₃H₃N (likely corresponding to acrylonitrile) and HNCO ranged in our study from 3.6-6.4 mg kg⁻¹ and BDL-11 mg kg⁻¹, respectively. Emission factors of C₃H₃N in the current study are lower than those observed during open burning (e.g., ~10-90 mg kg⁻¹ (Akagi et al., 2013)), as expected based on the lower acetonitrile emission factors observed in the current study and the findings of Coggon et al. (2016).”

Other Comments

Line 45: The descriptor “residential wood combustion” is unclear. Other studies have investigated the emissions from fuels typically burned in stoves (e.g. Douglas Fir, Stockwell 2015). To avoid confusion, please specify that you are speciating wood combustion emissions from commercial stoves.

The text has been modified as follows to specify that wood combustion emissions were speciated from commercial stoves (Page 3, lines 44-46): “Although two studies have speciated a large fraction of the NMOG mass emitted during residential wood combustion in commercial burners…”

Line 76: Please provide more details about the burner. Is the appliance fitted with a catalyst or secondary combustion zone? A description or schematic would be helpful for other researchers studying the emissions from other wood burners.

The burner was manufactured in 2009 and is not fitted with a catalyst or other emission control device. There is no secondary combustion zone. A photograph of the burner was added to the SI (new Figure S1) and a description of the burner was added to the main text (Page 4, lines 77-78): “…a residential wood burner (Figure S1; single combustion chamber, operated in single batch mode; Avant, 2009, Attika)…”

Line 90-91 What kind of lights are used to photolyze HONO? Can the authors provide flux measurements (or cite a source containing this information)?
In the chamber, HONO is photolyzed using 40 UV lights of 90-100 W (Cleo Performance, Philips) (Page 5, lines 98-99). Emission spectra of these lights, as well as inferred NO$_2$ and HONO photolysis rates for a similar set-up to the current study, can be found in Platt et al. (2013): Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, Atmos. Chem. Phys. 13, 9141-9158, 2013. This reference has been added to the manuscript.

**Line 91:** How do these levels of NO$_x$ compare to those from other biomass burning sources? NO$_x$ will also depend on fuel composition (e.g. Burling et al. 2010). Furthermore, how do NO$_x$ levels change after initiating the photolysis of HONO? Did the authors also measure ozone? If so, how much was formed as a result of photochemical processing? I believe these conditions are important to discuss, especially for future studies focused on biomass burning aging.

For NO$_x$, the primary EFs ranged from ~0.5-0.7 g kg$^{-1}$ (~160-350 ppbv in the chamber (mainly NO); no primary measurement available for experiment 1), which are much lower than literature for open burning (Stockwell et al., 2015 from open biomass burning of ponderosa pine (~2.5 g kg$^{-1}$) and black spruce (~5 g kg$^{-1}$)). Lower NO$_x$ (and N-containing NMOGs) EFs are expected due to the lower nitrogen content of the fuel used compared to open burning (Coggon et al., 2016). Upon aging, NO$_x$ increased to ~250-380 ppbv after reaching OH exposures of ~$(4.5-5.5) \times 10^7$ molec cm$^{-3}$ h, due to HONO photolysis. We have to note that NO$_x$ was measured using a chemiluminescence analyzer, and therefore the aforementioned concentrations should be considered as upper estimates, as the measurements are affected by NO$_y$ species (especially nitric acid).

Considering these high NO$_x$ values and the levels of measured reactive NMOGs in the beginning of the experiments (NMOG/NO$_x$ ratios of ~1-10), O$_3$ production is favored. For these experiments, we did not measure O$_3$ concentrations. However, previous measurements conducted under similar conditions indicate an initial O$_3$ production with aging. After an initial increase, O$_3$ concentrations significantly decrease due to the decrease of NMOG/NO$_x$ ratios (NMOG consumption and NO$_x$ increase with HONO photolysis).

The primary NO$_x$ values were added to the manuscript in a new table in the SI (Table S1), which includes other experimental parameters, as suggested by the other Referee. The following was added to the main text (Page 5, line 88): “Experimental parameters and primary emission values are summarized in Table S1.” and (Page 5, lines 94-96): “Levels of NO$_x$ in the chamber prior to aging range from ~160-350 ppbv and increases to ~250-380 ppbv after reaching OH exposures of ~$(4.5-5.5) \times 10^7$ molec cm$^{-3}$ h (NO$_x$ data unavailable for experiment 1).”

**Section 3.2.** The discussion about burn variability is much appreciated. Can the authors propose reasons for these differences? The tight reproducibility of MCE makes me think it’s not necessarily burning efficiency. Could there also be variability in how the burner operates that could lead to these differences (e.g. temperature)? Syc et al. observed significantly different emission factors of PAHs from a commercial burner when burning lignite at various temperatures. Hansson et al. (2004) observed differences in nitrogen NMOG distributions as a function of temperature for the pyrolysis of bark and other biomass sources. I would imagine that similar effects could be true for the combustion of beech wood.
We agree with the Referee that MCE, which is very similar in all experiments, is unlikely to be the cause of the difference in emission profiles between the experiments. As great care was taken to replicate each burn as closely as possible (e.g., similar starting wood mass, number of logs/kindling pieces and wood arrangement prior to ignition) and experimental conditions (e.g., dilution factors), there is no obvious explanation for the inter-experimental variability. The burner was housed in an uninsulated building and, as suggested, the variability could be due to effects of differences in outdoor temperature on the burner which would influence the combustion rate. Each fire was allowed to burn for 15-20 minutes prior to injecting emissions into the smog chamber, which allowed the burner to warm up, however, we did not make temperature measurements in the burner or chimney and temperature differences may have remained. The discussion on inter-burn variability was expanded to include these points (Page 13, lines 262-266): “The burner is housed in an uninsulated building and the emission profile variability could be due to effects of outdoor temperature variability on the burner. For example, emission profiles from burning lignite and pyrolysis of bark and other biomass sources have been shown to vary with burn temperature (Hansson et al., 2004; Šyc et al., 2011).”

Fig. 4: I assume that each panel is the temporal evolution of gas-phase species from each aging experiment. Is that correct? Please clarify.

Each panel corresponds to the temporal evolution for a single experiment. The figure legend has been modified, “…Temporal evolution of gas-phase species categorized by functional group throughout aging in the smog chamber for experiments 1-5 (a-e).”

References:


Anonymous Referee #2

This paper presents measurements of gas-phase species emitted from combustion of beech in a ‘modern’ residential heating stove in both fresh and aged states. Five replicate laboratory experiments were conducted in which emissions from a steady flaming combustion were sampled into a laboratory smog chamber, from which there were sampled for both a primary characterization period and during oxidation by OH formed via HONO photolysis. The use of replicate experiments is useful, as it assesses the extent to which emissions vary even within narrowly controlled circumstances – as it turns out, quite a bit. Interestingly, many of the emissions of concern (CO, OA, BC) are quite consistent across tests, as is the SOA produced during aging. In contrast, the composition and emission factors of NMOG varied substantially, with two tests having markedly different NMOG emissions. The evolution of NMOG is described in which many identified species show the expected decay with OH oxidation, while other species (acids, other O-containing species) showed enhancement.

This paper is clearly written and the measurements and analysis appear to be of high quality. This topic is of great interest to the readership of ACP as it provides important insights into the composition and evolution of an important class of biomass burning emissions. Below I have highlighted several points that would like to see addressed in revisions. The main focus of my comments is on the difference between the two sets of experiments – I would like to see a bit more discussion of the conditions that lead to these differences and how the two ‘anomalous’ experiments (#2, #3) differ from the others. This seems to be a key point, and while the differences are discussed, there’s little investigation of what might have influenced this difference. For example, the fuel consumed was nearly half during these experiments than the others, why? One general comment is that I was really required to read the other Bruns et al. 2016 paper in order to understand and interpret these results. While I understand that the authors split these aspects of the reporting of the project to avoid a cumbersome manuscript, I would like to see this one ‘stand alone’. So, at the least I would suggest that a table of basic test parameters (like Table 1 in Bruns et al 2016) be included, perhaps in the SI. Another general comment is that there is a bit of an over-emphasis on differences between results observed here (one fuel, one combustion condition) and observations more generally. In most cases, these comparisons are appropriately caveated, but in some cases the generalizations are a bit sweeping (e.g. Line 283) – I ask the authors to give this a once over to ensure that these results, while certainly providing key insights and data, are not over-extrapolated. Finally, I second many of the concerns/questions of the first referee.

Once these general and specific points have been addressed, I recommend the manuscript for publication in ACP.

We have expanded the discussion on the differences between the two sets of experiments (2 and 3 vs 1, 4 and 5) as described in detail below. We agree that this manuscript should ‘stand-alone’ and have taken the suggestion of the Referee to add a table with the experimental parameters to the SI (new Table S1). We have also modified the text to ensure the insights from these data are not over-extrapolated, as described below. The responses to the concerns/questions of the first Referee are detailed above.
Specific points

I am a bit confused by Table 2 – this indicates acetonitrile as the only N-containing species, but EF of acetonitrile is ~10 times lower than that for N-containing species? Is the rest of this mass contributed by un-identified compounds? It also doesn’t seem as if N-containing species contribute 20-30 mg/kg to NMOG mass on Figure 1, but it would be hard to see there. N-containing species were higher for Expts. 2-3, but aerosol-phase nitrate was substantially lower (even accounting for lower fuel consumption) (Bruns et al. 2016). Were there any other notable differences? E.g. NOx levels? Have you examined secondary nitrate formation during aging?

There are 14 N-containing species which contribute to this category and it is correct that 13 of these N-containing species have not been structurally assigned (the exception is acetonitrile). One reason for the lack of assignments is a scarcity of published data on N-containing emissions from residential wood combustion compared to emissions of other classes of compounds. However, an educated guess can be made about several of these compounds based on reasonable structures (e.g., C\textsubscript{3}H\textsubscript{3}N likely corresponds to acrylonitrile, as discussed in the response to the other Referee). A brief discussion and the range of emission factors observed for C\textsubscript{3}H\textsubscript{3}N and HNCO (in the O- and N-containing category), two compounds of interest in open biomass burning emissions, have been added to the text (Page 14, lines 288-300; see response to other Referee). Future work to identify more N-containing species emitted during residential wood combustion would be informative, similar to the recent work on identifying N-containing emissions from open biomass burning (i.e., Coggon et al., 2016, Stockwell et al., 2015). The majority of the mass contributing to the N-containing class is distributed among several compounds and the total mass of N-containing species is the lowest of all classes, which is likely why it is difficult to see these individual N-containing species in Figure 1.

N-containing species were higher and aerosol phase nitrate lower in experiments 2 and 3 compared to experiments 1, 4 and 5, however, there was no notable difference in NO\textsubscript{x} emissions between experiments 2 and 3 (~0.5 and 0.7 g kg\textsuperscript{-1}, respectively) compared to experiments 1, 4 and 5 (~0.5 and 0.6 g kg\textsuperscript{-1}, respectively; NO\textsubscript{x} data not available for experiment 1). With aging, particulate nitrate (NO\textsubscript{3}) showed varied behavior; however, there is no trend between experiments 2 and 3 compared to experiments 1, 4 and 5. After correction for wall losses, NO\textsubscript{3} remains stable in experiment 1, NO\textsubscript{3} increases by ~15% of its primary value during initial aging and then remains stable in experiment 2, NO\textsubscript{3} decreases by ~10% of its primary value during initial aging and then remains stable in experiment 3, and NO\textsubscript{3} increases by ~15% of its primary value in experiments 4 and 5 and then slowly decreases with further aging. AMS measurements of NO\textsubscript{3} includes inorganic and organic species; however, characterization, including quantification, of organic nitrate species is challenging using aerosol mass spectrometry and more work is needed to investigate particulate organic nitrates from residential wood combustion. The presence of bark, twigs and leaves have recently been shown to influence the emission of N-containing species during burning (Coggon et al., 2016), however, no difference in fuel composition is expected between the experiments as all bark and twigs were removed prior to combustion. As described above in a response to other Referee, differences in emission profiles may have been due to differences in ambient temperature effecting burner operation leading to differences in combustion rates.
L255 – Figure 2 is just mentioned here, and this could bear a bit more discussion and the differences between experiments discussed a bit further. One thing that stands out about these two experiments (2, 3) is that the CO2 loading in the chamber was substantially (almost half) lower than the other three experiments (despite the fact that the MCEs and many other quantities are essentially the same. If the injection time and dilution conditions were the same, this suggests that perhaps the combustion rate was lower (which would probably be indicated by lower flue temperature). Are there any other contextual or operational details that were different?

This point was raised by the other Referee as well. The MCE, which is very similar in all experiments, is unlikely to be the cause of the difference in emission profiles between the experiments. As great care was taken to replicate each burn as closely as possible (e.g., similar starting wood mass, number of logs/kindling pieces and wood arrangement prior to ignition) and experimental conditions (e.g., dilution factors), there is no obvious explanation for the inter-experimental variability. The burner was housed in an uninsulated building and, as suggested by the both Referee, the variability could be due to effects of differences in outdoor temperature on the burner and chimney which would reduce the combustion rate. Each fire was allowed to burn for 15-20 minutes prior to injecting emissions into the smog chamber, which allowed the burner to warm up, however, we did not make temperature measurements in the burner or chimney and temperature differences may have remained. The discussion on inter-burn variability was expanded to include these points (Page 13, lines 262-266): “The burner is housed in an uninsulated building and the emission profile variability could be due to effects of outdoor temperature variability on the burner. For example, emission profiles from burning lignite and pyrolysis of bark and other biomass sources have been shown to vary with burn temperature (Hansson et al., 2004; Šyc et al., 2011).”

L283 – This is too broad/definitive of a statement to make based on the narrow set of conditions tested here.

The text has been modified as follows (Page 14, lines 304-306): “…making acetonitrile a poor marker for residential wood combustion under these burning conditions. Coggon et al. (2016) concluded that acetonitrile may not be a good tracer for residential burning in urban areas.”

L317-319 – It would be useful/instructive to attempt a mass balance on the NMOG and SOA loadings to estimate how much of the measured NMOG may be ending up in the condensed phase in your experiments.

The work detailed in our previous publication on these experiments provides the first quantitative closure of the mass balance of the gas-phase species contributing to SOA (Bruns et al., 2016). We determined that the conversion of NMOGs traditionally included in models to SOA account for only ~3-27% of the observed SOA, whereas ~84-116% of the SOA can be explained by inclusion of non-traditional precursors, including naphthalene and phenol. The text was modified as follows (Page 16, lines 343-346): “Previous investigation of these experiments determined that the conversion of NMOGs traditionally included in models to SOA accounts for only ~3-27% of the observed SOA, whereas ~84-116% of the SOA is explained by inclusion of non-traditional precursors, including naphthalene and phenol (Bruns et al., 2016).”
L358 – Were terpenes actually quantified? I don’t expect much from birch wood, but if you measured them (or found them BDL) this should be noted.

As expected from previous studies (e.g., Schauer et al., 2001), monoterpenes were below the detection limit in all experiments. Isoprene emissions (Table 2) were also relatively low, although above the detection limit. This information has been added to the manuscript (Page 18, lines 394-395): “Monoterpene concentrations are below the detection limit in all experiments and isoprene emissions are relatively low (Table 2).”

L362 – ‘Good agreement’ is a bit vague, there is not-great agreement in panels c) and f). Could this indicate possibly misattribution of these compounds? For this figure, it would be helpful to show smoothed data (and probably a log y-axis) to make this a bit more readable.

We have modified the Figure (now Figure S3) to show the smoothed data (10 s data smoothed to 5 min moving average) to improve readability. We have also added some additional discussion of this Figure to address the Referee’s comments that the agreement is better for some compounds (i.e., panels a, b, c, e, g, h) compared to others (i.e., panels d, f and i) (Page 19, lines 400-408): “There is generally good agreement between the observed and calculated decay for each compound which supports the structural assignment of each ion. For 2-methoxyphenol and 2,6-dimethoxyphenol (Figure S3 f and i, respectively), the agreement between the observed and calculated decays is not as good as for the other compounds, with slower decays than predicted. This discrepancy may be due to fragmentation of related compounds to form 2-methoxyphenol and 2,6-dimethoxyphenol in the instrument or formation of these compounds in the chamber during oxidation. For o-benzeneediol, the decays are initially faster than expected and then become slower with increased aging, possibly due to the presence of isomers with different reaction rates with respect to OH.”

L365-370 - Somewhat confusing lead-in to discussion of Figure 3, as discussion emphasizes differences between experiments and this figure shows averages across all experiments - may make sense to just discuss this result then discuss inter-experiment differences (using Fig. 2)

We agree with the Referee and have introduced Figure 3 in the preceding paragraph and then discussed the inter-experiment differences on SOA formation potential using Figure 2 in the next paragraph (Pages 18-20, lines 396-433): “We have previously identified the compounds contributing to the majority of the SOA formed during these experiments (Bruns et al., 2016). The average EF for each of these species is shown in Figure 3. Figure S3 shows the observed decay of the SOA precursors contributing the most to SOA formation during aging in the chamber compared to the expected decay based on the OH concentration in the chamber and the reaction rate with respect to OH. There is generally good agreement between the observed and calculated decay for each compound which supports the structural assignment of each ion. For 2-methoxyphenol and 2,6-dimethoxyphenol (Figure S3 f and i, respectively), the agreement between the observed and calculated decays is not as good as for the other compounds, with slower decays than predicted. This discrepancy may be due to fragmentation of related compounds to form 2-methoxyphenol and 2,6-dimethoxyphenol in the instrument or formation of these compounds in the chamber during oxidation. For o-benzeneediol, the decays are initially faster than expected and then become slower with increased aging, possibly due to the presence of isomers with different reaction rates with respect to OH.
As described above, the overall primary emission profiles, as well as total NMOG emissions, vary considerably for experiments 2 and 3 compared to experiments 1, 4 and 5, with considerably higher total NMOG emissions in experiments 2 and 3. To determine the impact of the high NMOG emission experiments (2 and 3) compared to the lower NMOG emission experiments (1, 4 and 5) on SOA formation potential, individual SOA precursors with published SOA yields are investigated. The SOA formation potential for each of these 18 compounds is determined as the product of the primary EF and the best estimate SOA yield determined from the literature, as determined previously (Bruns et al., 2016). The total SOA formation potential for each experiment is taken as the sum of the individual SOA formation potentials. Interestingly, the SOA formation potential is similar in all experiments and the average enhancement of SOA formation potential in experiments 2 and 3 compared to the average of experiments 1, 4 and 5 is insignificant (Figure 2), despite the considerably different total NMOG EFs.”

References

Characterization of gas-phase organics using proton transfer reaction time-of-flight mass spectrometry: fresh and aged residential wood combustion emissions

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Abstract

Organic gases emitted during the flaming phase of residential wood combustion are characterized individually and by functionality using proton transfer reaction time-of-flight mass spectrometry. The evolution of the organic gases is monitored during photochemical aging. Primary gaseous emissions are dominated by oxygenated species (e.g., acetic acid, acetaldehyde, phenol and methanol), many of which have deleterious health effects and play an important role in atmospheric processes such as secondary organic aerosol formation and ozone production.

Residential wood combustion emissions differ considerably from open biomass burning in both absolute magnitude and relative composition. Ratios of acetonitrile, a potential biomass burning marker, to CO are considerably lower (~0.09 pptv ppbv$^{-1}$) than those observed in air masses influenced by open burning (~1-2 pptv ppbv$^{-1}$), which may make differentiation from background levels difficult, even in regions heavily impacted by residential wood burning.

Considerable formic acid forms during aging (~200-600 mg kg$^{-1}$ at an OH exposure of (4.5-5.5)×10$^7$ molec cm$^{-3}$ h), indicating residential wood combustion can be an important local source for this acid, the quantities of which are currently underestimated in models. Phthalic anhydride, a naphthalene oxidation product, is also formed in considerable quantities with aging (~55-75 mg kg$^{-1}$ at an OH exposure of (4.5-5.5)×10$^7$ molec cm$^{-3}$ h). Although total NMOG emissions vary by up to a factor of ~9 between burns, SOA formation potential does not scale with total NMOG emissions and is similar in all experiments. This study is the first thorough characterization of both primary and aged organic gases from residential wood combustion and provides a benchmark for comparison of emissions generated under different burn parameters.
1 Introduction

Residential wood combustion is a source of gaseous and particulate emissions in the atmosphere, including a complex mixture of non-methane organic gases (NMOGs) (McDonald et al., 2000; Schauer et al., 2001; Hedberg et al., 2002; Jordan and Seen, 2005; Pettersson et al., 2011; Evtyugina et al., 2014; Reda et al., 2015). NMOGs impact climate (Stocker et al., 2013) and health (Pouli et al., 2003; Bølling et al., 2009) both directly and through the formation of products during atmospheric processing (Mason et al., 2001; Kroll and Seinfeld, 2008; Shao et al., 2009), which makes NMOG characterization critical. Although two studies have speciated a large fraction of the NMOG mass emitted during residential wood combustion in commercial burners (McDonald et al., 2000; Schauer et al., 2001), these studies relied on offline chromatographic approaches, which are time consuming in terms of sample preparation and analysis and can introduce both positive and negative artifacts (Nozière et al., 2015). Relatively recently, the proton transfer reaction mass spectrometer (PTR-MS) has emerged as a powerful tool for online quantification of atmospherically-relevant NMOGs (Lindinger et al., 1998; Jordan et al., 2009) eliminating many of the artifacts associated with offline approaches. NMOGs emitted during open burning of a variety of biomass fuels in the laboratory have been recently quantified using a high resolution proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS) (Stockwell et al., 2015) and select nominal masses were followed during aging of residential wood combustion emissions using a quadrupole PTR-MS (Grieshop et al., 2009a). However, a complete high-resolution characterization of residential wood combustion emissions has yet to be performed.

The quantities and composition of NMOGs emitted during residential wood combustion are highly dependent on a number of parameters including wood type, appliance type and burn
conditions, and as few studies have characterized these NMOGs (McDonald et al., 2000; Schauer et al., 2001; Hedberg et al., 2002; Jordan and Seen, 2005; Pettersson et al., 2011; Evtyugina et al., 2014; Reda et al., 2015), further work is needed to constrain emission factors, as highlighted in the recent review article by Nozière et al. (2015). Also, little is known about the evolution of NMOGs from residential wood combustion with aging.

In this study, we present results from the first use of a smog chamber and a PTR-ToF-MS to characterize primary and aged gaseous emissions from residential wood combustion in real-time. This novel approach allows for an improved characterization of NMOG emissions, particularly oxygenated NMOGs, which are a considerable fraction of the total NMOG mass emitted during residential wood combustion (McDonald et al., 2000; Schauer et al., 2001). This study focuses on a narrow set of burn conditions, namely the flaming phase of beech wood combustion, in order to generate as reproducible emissions as possible for a complementary investigation of the effects of parameters such as temperature on the emissions. While these experiments are a narrow representation of real-world conditions, this novel work provides a benchmark and direction for future wood combustion studies.

2 Methods

2.1 Emission generation and smog chamber operation

Beech (*Fagus sylvatica*) logs are combusted in a residential wood burner ([Figure S1; single combustion chamber, operated in single batch mode;](#) Avant, 2009, Attika) and emissions are sampled from the chimney through a heated line (473 K), diluted by a factor of ~8-10 using an ejector diluter (473 K, DI-1000, Dekati Ltd.) and injected into the smog chamber (~7 m³) through a heated line (423 K). Emissions are sampled during the stable flaming phase of
burn and modified combustion efficiencies (MCEs), defined as the ratio between CO\(_2\) and the sum of CO and CO\(_2\), range from 0.974-0.978 (Table 1).

Emissions are injected for 11-21 min and total dilution factors range from ~100-200. All experiments are conducted under similar conditions with starting wood masses in the burner of 2.9±0.3 kg and a wood moisture content of 19±2%. The smog chamber has an average temperature of 287.0±0.1 K and a relative humidity of 55±3% over all five experiments. Experimental parameters and primary emission values are summarized in Table S1. After characterization of the primary emissions, as described below, a single dose of d\(_9\)-butanol (2 µl, butanol-D9, 98%, Cambridge Isotope Laboratories) is injected into the chamber and a continuous injection of nitrous acid in air (2.3-2.6 l min\(^{-1}\), ≥99.999%, Air Liquide) into the chamber begins. The decay of d\(_9\)-butanol measured throughout aging is used to estimate hydroxyl radical (OH) exposures (Barmet et al., 2012). Nitrous acid produces OH upon irradiation in the chamber and is used to increase the degree of aging. Levels of NO\(_x\) in the chamber prior to aging range from ~160-350 ppbv and increases to ~250-380 ppbv after reaching OH exposures of ~(4.5-5.5)×10\(^7\) molec cm\(^{-3}\) h (NO\(_x\) data unavailable for experiment 1). The small continuous dilution in the chamber during aging due to the constant nitrous acid injection is accounted for using CO as an inert tracer. The chamber contents are irradiated with UV light (40 lights, 90-100 W, Cleo Performance, Philips) (Platt et al., 2013) for 4.5-6 h (maximum OH exposures of (4.7-6.8)×10\(^7\) molec cm\(^{-3}\) h which corresponds to ~2-3 days of aging in the atmosphere at an OH concentration of 1×10\(^6\) molec cm\(^{-3}\)). Reported quantities of aged species are taken at OH exposures of (4.5-5.5)×10\(^7\) molec cm\(^{-3}\) h (Table 1; ~1.9-2.3 days of aging in the atmosphere at an OH concentration of 1×10\(^6\) molec cm\(^{-3}\)) (Barmet et al., 2012).

2.2 Gas-phase analysis
NMOGs with a proton affinity greater than that of water are measured using a PTR-ToF-MS (PTR-ToF-MS 8000, Ionicon Analytik GmbH) and CO₂, CO and CH₄ are measured using cavity ring-down spectroscopy (G2401, Picarro, Inc.). The PTR-ToF-MS operates with hydronium ion ([H₂O+H]⁺) as the reagent, a drift tube pressure of 2.2 mbar, a drift tube voltage of 543 V and a drift tube temperature of 90°C leading to a ratio of the electric field (E) and the density of the buffer gas (N) in the drift tube (reduced electric field, E/N) of 137 Townsend (Td). The transmission function is determined using a gas standard of six NMOGs of known concentration (methanol, acetaldehyde, propan-2-one, toluene, p-xylene, 1,3,5-trimethylbenzene; Carbagas). As the RH and temperature of the sampled air is similar in all experiments, changes in the detection efficiency of individual species are not expected.

PTR-ToF-MS data are analyzed using the Tofware post-processing software (version 2.4.5, TOFWERK AG, Thun, Switzerland; PTR module as distributed by Ionicon Analytik GmbH), running in the Igor Pro 6.3 environment (version 6.3, Wavemetrics Inc.). The minimum detection limit is taken as three standard deviations above the background, where the standard deviation is determined from the measurements of each ion in the chamber prior to emission injection. Isotopic contributions are constrained during peak fitting and are accounted for in reported concentrations. Possible molecular formulas increase with increasing m/z, making accurate peak assignments difficult in the higher m/z range. Mass spectral data from m/z 33 to m/z 130 are assigned molecular formulas, as well as the ¹⁸O isotope of the reagent ion and signal above m/z 130 corresponding to compounds previously identified during residential wood combustion (McDonald et al., 2000; Schauer et al., 2001; Hedberg et al., 2002; Jordan and Seen, 2005; Pettersson et al., 2011; Evtyugina et al., 2014; Reda et al., 2015). All signal above m/z 130...
is included in total NMOG mass quantification. Using this approach, ~94-97% of the total NMOG mass measured using the PTR-ToF-MS has an ion assignment.

The reaction rate constant of each species with the reagent ion in the drift tube is needed to convert raw signal to concentration. When available, individual reaction rate constants are applied to ions assigned a structure (Cappellin et al., 2012) (Table S24), otherwise a default reaction rate constant of $2 \times 10^{-9}$ cm$^3$ s$^{-1}$ is applied. For possible isomers, the reaction rate constant is taken as the average of available values. Approximately 60-70% of the total NMOG mass is comprised of compounds with known rate constants. NMOG signal is normalized to $[\text{H}_2^{18}\text{O}+\text{H}]^+$ to convert to concentration. Emission factors (EFs) normalize concentrations to the total wood mass burned (e.g., mg kg$^{-1}$ reads as mg of species emitted per kg wood burned) to facilitate comparison between experiments and are calculated as described previously (Andreae and Merlet, 2001; Bruns et al., 2015a).

PTR-ToF mass spectrometry is a relatively soft ionization technique generally resulting in protonation of the parent NMOG ([M+H]$^+$), although some compounds are known to produce other ions, for example through fragmentation or rearrangement (e.g., Baasandorj et al. (2015)). Reactions potentially leading to considerable formation of species besides [M+H]$^+$ are discussed in the Supplement. The extent to which reactions leading to ions other than [M+H]$^+$ occurs is dependent on instrument parameters such as $E/N$. The unknown relative contributions of various isomers makes it difficult to account for reactions generating ions besides [M+H]$^+$ and thus, no fragmentation corrections are applied. Emission factors of compounds likely to undergo extensive reaction to form products besides [M+H]$^+$ (i.e., methylcyclohexane (Midey et al., 2003), ethyl acetate (Baasandorj et al., 2015) and saturated aliphatic aldehydes (Buhr et al.,
Due to interferences, butenes \([\text{C}_4\text{H}_8+\text{H}]^+\) are not quantified.

### 3 Results and Discussion

#### 3.1 NMOG emissions

In all experiments, the largest EFs for a single gas-phase species correspond to CO\(_2\) (1770-1790 g kg\(^{-1}\)) and CO (27-30 g kg\(^{-1}\)) (Table 2), which are in good agreement with previous measurements from residential beech logwood combustion where CO\(_2\) EFs of ~1800 g kg\(^{-1}\) and CO EFs of ~20-70 g kg\(^{-1}\) were measured (Ozil et al., 2009; Schmidl et al., 2011; Kistler et al., 2012; Evtyugina et al., 2014; Reda et al., 2015). Methane is also emitted in considerable quantities (1.5-2.8 g kg\(^{-1}\)), similar to previously observed values for beech wood burning in fireplaces (0.5-1 g kg\(^{-1}\) (Ozil et al., 2009), however, at generally lower levels than total NMOGs (1.5-13 g kg\(^{-1}\)). Total NMOG EFs from beech wood combustion have not been previously reported, but values are similar to studies of residential wood stove burning of different hardwoods which have attempted a detailed quantification of total NMOGs, such as McDonald et al. (2000) (6.2-55.3 g kg\(^{-1}\) for a hardwood mixture) and Schauer et al. (2001) (6.7 g kg\(^{-1}\) for oak). Total NMOG quantities reported in this study refer to species quantified using the PTR-ToF-MS.

Although a large fraction of atmospherically-relevant organic gases are measured using the PTR-ToF-MS, some species are not quantitatively detected, including those with a proton affinity less than water (i.e., small alkanes). Based on previous studies of residential burning, alkanes are estimated to contribute less than ~5% to the NMOG mass of either hard or softwood and the sum of alkenes and alkynes, some of which are quantifiable with the PTR-ToF-MS, are estimated to...
contribute less than ~15% to the total measured NMOG mass (McDonald et al., 2000; Schauer et al., 2001).

Figure 1 shows the primary NMOG mass spectrum for each experiment classified by NMOG functionality and the fractional contribution of NMOG functional groups to the total NMOG mass. EFs for individual compounds are presented in Table 2. For ease of reading, nominal \( m/z \)s are presented in the text and figures, however, monoisotopic \( m/z \)s for all identified species can be found in Tables 2 and S32. Separation of isobaric species is possible using the PTR-ToF-MS, however, isomers remain indistinguishable. Quantities of gas-phase species generated during residential wood combustion depend on a variety of parameters, such as type of burner and wood species. However, many compounds are commonly emitted and structures are assigned to observed ions based on previously identified species (McDonald et al., 2000; Schauer et al., 2001; Hedberg et al., 2002; Jordan and Seen, 2005; Pettersson et al., 2011; Evtyugina et al., 2014; Reda et al., 2015). A few small, unambiguous ions are also assigned a structure, including methanol, formic acid and acetonitrile. Approximately 70% of the total NMOG mass measured using the PTR-ToF-MS is assigned a structure based on this method.

NMOGs are categorized by functional groups including: oxygenated, total C\(_x\)H\(_y\), nitrogen-containing and other. Oxygenated subcategories include: acids (comprised of non-aromatic acids), carbonyls (comprised of non-aromatic carbonyls), oxygenated aromatics (not including furans), furans, O-containing (comprised of structurally unassigned oxygenated compounds and multifunctional oxygenated compounds) and O- and N-containing (comprised of species containing both oxygen and nitrogen atoms). Species categorized as N-containing contain no oxygen atoms. Total C\(_x\)H\(_y\) subcategories include: aromatic hydrocarbons, and non-aromatic and structurally unassigned species (referred to as C\(_x\)H\(_y\) in the text and figures). Higher molecular
weight species lacking an ion assignment are categorized as “other”. In the case of possible isomers, ions are categorized according to the species most likely to dominate based on previous studies (McDonald et al., 2000; Schauer et al., 2001; Hedberg et al., 2002; Jordan and Seen, 2005; Pettersson et al., 2011; Evtyugina et al., 2014; Reda et al., 2015).

Oxygenated species contribute ~68-94% to the total primary NMOG mass, which has important atmospheric implications due to the role of these compounds in photochemical reactions, for example by altering O₃ and peroxide formation (Mason et al., 2001; Shao et al., 2009). McDonald et al. (2000) and Schauer et al. (2001) previously observed the dominance of oxygenated NMOGs during residential burning of other wood types, whereas Evtyugina et al. (2014) found that benzene and benzene derivatives contributed 59% to the total measured NMOGs, compared to only 26% from oxygenated compounds for residential burning of beech wood in a woodstove. However, Evtyugina et al. (2014), as well as McDonald et al. (2000) and Schauer et al. (2001), did not include emissions from all lower molecular weight NMOGs, such as acetic acid. Oxygenated NMOGs are also reported as a large fraction of NMOGs emitted during open burning of many biomass fuels (Gilman et al., 2015; Stockwell et al., 2015).

Acids are the most abundant subclass of species in all experiments with an average EF of 2000±2000 mg kg⁻¹ and acetic acid ([C₂H₄O₂⁺H]+ at nominal m/z 61) is the most highly emitted compound in all experiments. In addition to acetic acid, [C₃H₆O₂⁺H]+ can correspond to glycolaldehyde, however, Stockwell et al. (2015) found that acetic acid contributes ~75-93% to [C₂H₄O₂⁺H]+ during open burning of black spruce (Picea mariana) and ponderosa pine (Pinus ponderosa) and thus, it is expected that this ion is also largely attributable to acetic acid in the current study. Acetic acid and formic acid ([CH₂O₂⁺H]+ at nominal m/z 47) are the most abundant carboxylic acids in the atmosphere and are important contributors to atmospheric
acidity (Chebbi and Carlier, 1996). However, the sources of these acids are poorly understood (Paulot et al., 2011) and data on their EFs from residential wood combustion are relatively unknown. The high acetic acid EFs found here indicate that residential wood combustion can be an important local source of this acid. Interestingly, the enhancement of acetic acid ($\Delta C_2H_4O_2$) over background levels relative to CO enhancement ($\Delta CO$) in the current study ranges from ~6 to 80 pptv ppbv$^{-1}$ (Table 1), which is much higher than the average 0.58 pptv ppbv$^{-1}$ (sum of gas and aerosol phase) measured in an Alpine valley heavily impacted by residential wood combustion in winter (Gaeggeler et al., 2008). Further work is needed to investigate the source of this discrepancy, as limited ambient measurements are available from regions heavily impacted by residential wood combustion. However, it is possible that the ambient measurements were dominated by emissions produced during poor burning conditions (e.g., starting phase) where CO EFs are expected to be higher than during the stable burning phase investigated in the current study.

The sum of oxygenated and non-oxygenated aromatic compounds contribute ~7-30% (800±300 mg kg$^{-1}$) to the total primary NMOG mass with benzene ([C$_6$H$_6$+H]$^+$ at nominal m/z 79), phenol ([C$_6$H$_5$O+H]$^+$ at nominal m/z 95), and naphthalene ([C$_{10}$H$_8$+H]$^+$ at nominal m/z 129) as the three most dominant species. Oxidation products of aromatic species are the largest contributors to residential wood combustion SOA in this study (Bruns et al., 2016) and both aromatic and related oxidation products are of interest due to their particularly deleterious effects on health (Fu et al., 2012).

For the other functional group categories, carbonyl and alcohols contribute ~8-12% (600±600 mg kg$^{-1}$) and ~3-5% (300±300 mg kg$^{-1}$), respectively, to the total NMOG mass. In general, the most highly emitted carbonyl compound is acetaldehyde ([C$_2$H$_4$O+H]$^+$ at nominal m/z 45).
Methanol ([\text{CH}_3\text{OH}+\text{H}]^+ \text{ at nominal } m/z \ 33) \text{ is the most highly emitted alcohol, although other acyclic alcohols can undergo extensive fragmentation in the mass spectrometer. Furans are only a minor contributor to the total primary NMOG mass, contributing } \sim3-5\% \ (300\pm300 \text{ mg kg}^{-1}), \text{ but are of potential interest as several furans were recently identified as SOA precursors (Gómez Alvarez et al., 2009) and possible open biomass burning markers (Gilman et al., 2015).}

### 3.2 Burn variability

Although the same compounds are emitted during all burns, there is variability in EFs between experiments despite efforts to replicate burns as closely as possible and the fact that the MCE for each experiment falls within a narrow range (0.974-0.978) (Table 1). Experiments 2 and 3 show marked differences in total NMOG EFs and NMOG composition compared to experiments 1, 4 and 5. For example, the total NMOG EF is \sim9 times higher in experiment 2 compared to experiment 5 (Table 2). Acetic acid EFs vary by a factor of \sim15 between burns, with high emissions in experiments 2 and 3 relative to experiments 1, 4 and 5. The total emission of oxygenated species also correlates with acetic acid emissions, with total oxygenated EFs considerably higher in experiments 2 and 3 than in experiments 1, 4 and 5. In contrast, aromatic hydrocarbons and C\text{\textsubscript{x}}H\text{\textsubscript{y}} EFs show no correlation with total oxygenated species or acetic acid EFs. Interestingly, differences in black carbon EFs, primary organic aerosol EFs and primary organic aerosol mass to black carbon ratios are also not observed between these two groupings of experiments (2, 3 and 1, 4, 5), as presented previously (Bruns et al., 2016). Enhancements in the average EF for the different functional groups in experiments 2 and 3 relative to experiments 1, 4 and 5 are shown in Figure 2.
The differences in EFs due to inter-burn variability illustrate the difficulty in constraining EFs from residential wood combustion. The burner is housed in an uninsulated building and the emission profile variability could be due to effects of outdoor temperature variability on the burner. For example, emission profiles from burning lignite and pyrolysis of bark and other biomass sources have been shown to vary with burn temperature (Hansson et al., 2004; Šyc et al., 2011). Further work to constrain the possible range of EFs generated under different conditions is critical for improving model inputs. EFs are also dependent on factors such as appliance type and fuel loading and further work is needed to characterize the emissions and the evolution of these emissions with aging generated from burning of different wood types and under different burn parameters.

### 3.3 Biomass burning tracers

Individual compounds emitted exclusively or in large quantities during biomass burning are of interest for source apportionment and compounds contributing to SOA formation are of particular interest for climate and health (Figure 3). Acetonitrile is used as an ambient gas-phase marker for open biomass burning (de Gouw et al., 2003; Singh et al., 2003). In the current experiments, acetonitrile EFs are relatively low (3.5±0.3 mg kg\(^{-1}\)) compared to open biomass burning (~20-1000 mg kg\(^{-1}\)) (Yokelson et al., 2008; Yokelson et al., 2009; Akagi et al., 2013; Stockwell et al., 2015), likely due to different burn conditions (e.g., oxygen availability). The enhancements of acetonitrile over background levels relative to CO enhancement, ΔCH\(_3\)CN/ΔCO, are ~0.08-0.1 pptv ppbv\(^{-1}\) (Table 1). This is slightly lower than the only previously published residential wood combustion measurements (0.1 to 0.8 pptv ppbv\(^{-1}\)) (Grieshop et al., 2009a), but is much lower than ΔCH\(_3\)CN/ΔCO measurements in ambient air masses impacted by open biomass burning (~1-2 pptv ppbv\(^{-1}\)) (Holzinger et al., 1999; Andreae...
and Merlet, 2001; Christian et al., 2003; de Gouw et al., 2003; Jost et al., 2003; Holzinger et al., 2005; de Gouw et al., 2006; Warneke et al., 2006; Yokelson et al., 2008; de Gouw et al., 2009; Yokelson et al., 2009; Aiken et al., 2010; Akagi et al., 2013). However, $\Delta$CH$_3$CN/$\Delta$CO during open burning has been shown to depend strongly on fuel type; Stockwell et al. (2015) observed $\Delta$CH$_3$CN/$\Delta$CO values from 0.0060-7.1 pptv ppbv$^{-1}$ for individual open burns of different biomass types in the laboratory. In agreement with the current study, ambient measurements of acetonitrile made in Colorado (USA) were not associated with fresh residential burning emissions (Coggon et al., 2016). Lower ambient measurements of nitrogen-containing NMOGs (including acetonitrile) during residential burning compared to open burning were attributed to the generally lower nitrogen content in fuels burned residually (Coggon et al., 2016). Lower nitrogen content of the fuel is likely a contributor to the relatively low acetonitrile emissions in the current study.

The primary emission factors of other nitrogenated species, such as C$_3$H$_3$N (likely corresponding to acrylonitrile) and HNCO ranged in our study from 3.6-6.4 mg kg$^{-1}$ and BDL-11 mg kg$^{-1}$, respectively. Emission factors of C$_3$H$_3$N in the current study are lower than those observed during open burning (e.g., ~10-90 mg kg$^{-1}$ (Akagi et al., 2013)), as expected based on the lower acetonitrile emission factors observed in the current study and the findings of Coggon et al. (2016)."

Further work is needed to investigate CH$_3$CN emissions from residential burning of other wood types, as well as emissions during other burning phase (e.g., smoldering). However, these low enhancements may be difficult to differentiate from ambient background levels, making acetonitrile a poor marker for residential wood combustion under these burning conditions.
Coggon et al. (2016) concluded that acetonitrile may not be a good tracer for residential burning in urban areas.

The interference from isobaric compounds when quantifying acetonitrile using a PTR-MS is an important consideration when high resolution data are not available. Previously, several studies have determined this interference is minimal during open biomass burning (de Gouw et al., 2003; Warneke et al., 2003; Christian et al., 2004; Warneke et al., 2011). Recently, Dunne et al. (2012) quantified interferences with acetonitrile measurements in polluted urban air using a quadrupole PTR-MS and found contributions of 5-41% to \textit{m/z} 42 from non-acetonitrile ions including: \([\text{C}_3\text{H}_6]^+\) and the \(^{13}\text{C}\) isotope contribution from \([\text{C}_3\text{H}_5]^+\). In the current study, in addition to contributions from \([\text{C}_3\text{H}_6]^+\) and the isotopic contribution from \([\text{C}_3\text{H}_5]^+\), \(~30\text{-}50\%\) of the total signal at \textit{m/z} 42 is due to \([\text{C}_2\text{H}_2\text{O}]^+\), which is presumably a fragment from higher molecular weight species. The total contribution to \textit{m/z} 42 from species besides acetonitrile is \(~70\text{-}85\%\).

Although an investigation into the effects of the PTR-MS operating conditions (e.g., \([\text{O}_2]^+\) signal from ion source, \(E/\text{N}_a\) affecting fragmentation) is outside the scope of the current study, the possibility of considerable non-acetonitrile signal at \textit{m/z} 42 should be taken into consideration when using nominal mass PTR-MS data to quantify acetonitrile from residential wood combustion.

Methanol is also used to identify air masses influenced by open biomass burning and enhancement over background levels relative to CO enhancement (\(\Delta\text{CH}_3\text{OH}/\Delta\text{CO}\)) is typically \(~1\text{-}8\text{ pptv ppbv}^{-1}\) in ambient and laboratory measurements of fresh open biomass burning emissions (Holzinger et al., 1999; Goode et al., 2000; Andreae and Merlet, 2001; Christian et al., 2003; Yokelson et al., 2003; Singh et al., 2004; Tabazadeh et al., 2004; Holzinger et al., 2005; de Gouw et al., 2006; Gaeggeler et al., 2008; Yokelson et al., 2008; Yokelson et al., 2009; Akagi et
al., 2013; Stockwell et al., 2015; Müller et al., 2016). Here, we find similar values ranging from ~2-20 pptv ppbv$^{-1}$ (Table 1), in agreement with Gaeggeler et al. (2008) who measured a $\Delta$CH$_3$OH/$\Delta$CO value of 2.16 pptv ppbv$^{-1}$ in an Alpine valley heavily impacted by residential wood combustion emissions in winter.

### 3.4 Chamber studies of NMOG aging

Previous investigations of aged residential wood combustion emissions have largely focused on the evolution of the aerosol phase (Grieshop et al., 2009a; Grieshop et al., 2009b; Hennigan et al., 2010; Heringa et al., 2011; Bruns et al., 2015a; Bruns et al., 2015b; Bruns et al., 2016) and little is known about the evolution of the gas phase. The evolution of the NMOG functional group categories with increasing OH exposure is shown in Figure 4. Figure 5 shows the absolute change in mass spectral signal between the aged and primary NMOG quantities. Although an increase in NMOG mass could be expected with aging due to oxygenation, total NMOG mass decreases by ~5-30% at an OH exposure of $(4.6-5.5) \times 10^7$ molec cm$^{-3}$ h relative to the primary emissions in experiments 1-4, likely due to the conversion of species from the gas to particle phase, the mass of which increased considerably with aging (Bruns et al., 2016), and the formation of gas-phase species not quantified here (e.g., formaldehyde). Previous investigation of these experiments determined that the conversion of NMOGs traditionally included in models to SOA accounts for only ~3-27% of the observed SOA, whereas ~84-116% of the SOA is explained by inclusion of non-traditional precursors, including naphthalene and phenol (Bruns et al., 2016). The total NMOG mass increases slightly, by ~5%, in experiment 5. Quantities of individual NMOGs and NMOG functional group categories after reaching an OH exposure of $(4.6-5.5) \times 10^7$ molec cm$^{-3}$ h are presented in Table S32. In addition to gas to particle phase partitioning and formation of gas-phase species not quantified here, a decrease in NMOG mass...
with aging could also be due to losses of gas-phase species to the chamber walls (Zhang et al., 2014; Bian et al., 2015). Measurements of NMOGs in the chamber prior to aging are stable, indicating that the chamber walls are not a sink for NMOGs, but rather that NMOGs are in equilibrium with the chamber walls, particles and the gas phase. Zhang et al. (2014) show that the rate of NMOG wall loss is proportional to seed aerosol concentration and OH concentration, both of which were relatively high in the current experiments (Table S1; OH concentrations were $\sim1.4\times10^7$ molec cm$^{-3}$). Under these experimental conditions, NMOG wall losses are not expected to be large. Future studies are needed to investigate vapor wall loss of residential wood combustion emissions during aging.

Subcategories of oxygenated species behave differently with aging. For example, total quantities (mg kg$^{-1}$) of oxygenated aromatic species decrease by factors of $\sim$7-15 and furan quantities decrease by factors of $\sim$4-9, whereas all other oxygenated subcategories, as well as N-containing species, remain within a factor of 2 of primary values at an OH exposure of $(4.6\text{-}5.5)\times10^7$ molec cm$^{-3}$ h. Aromatic hydrocarbons and C$_x$H$_y$ quantities decrease with aging by factors of $\sim$1.5-3. The large decreases in oxygenated aromatic species and furans illustrate the highly reactive nature of these species with respect to OH. The evolution of the bulk NMOG elemental composition during aging is shown in Figure S24 in the Supplement.

In all experiments, formic acid quantities increase considerably with aging (by factors of $\sim$5-50), as does [C$_4$H$_2$O$_3$+H]$^+$ at nominal $m/z$ 99 (by factors of $\sim$2-3), which likely corresponds to maleic anhydride, both of which are formed during the oxidation of aromatic species among other compounds (Bandow et al., 1985; Sato et al., 2007; Praplan et al., 2014). However, the fragment resulting from the loss of water from maleic acid cannot be distinguished from maleic anhydride using the PTR-ToF-MS. Formic acid is underestimated in models, likely due to
missing secondary sources (Paulot et al., 2011) and these results indicate that aging of residential
wood combustion emissions can result in considerable secondary formic acid production. The
signal at $m/z$ 149, corresponding to $[C_8H_4O_3+H]^+$, increases by factors of ~2-7 with aging. This
ion likely corresponds to phthalic anhydride, which is a known naphthalene oxidation product
(Chan et al., 2009).

Acetic acid formation has been observed in some ambient, open biomass burning plumes with
aging (Goode et al., 2000; Hobbs et al., 2003; Yokelson et al., 2003), whereas not in others (de
Gouw et al., 2006) and a doubling of $m/z$ 61, likely dominated by acetic acid, was observed
during aging of residential burning emissions in a previous laboratory study (Grieshop et al.,
2009a). In the current study, no increase in the average acetic acid concentration relative to
$CO_{(g)}$ is observed (Table 1). Note that this implies production of secondary acetic acid that
compensates for the expected consumption of ~8-10% of primary acetic acid by reaction with
OH at an OH exposure of $(4.5-5.5)\times10^7$ molec cm$^{-3}$ h. These results indicate that acetic acid
from residential burning of beech wood is dominated by primary emissions of this species (Table
1). As with acetic acid, there are discrepancies in methanol behavior as open biomass burning
plumes undergo aging (Goode et al., 2000; Yokelson et al., 2003; Tabazadeh et al., 2004;
Holzinger et al., 2005; de Gouw et al., 2006; Akagi et al., 2013). As described by Akagi et al.
(2013), methanol enhancement has been hypothesized to correlate with terpene concentration
and here, methanol remains within ~1-20% of the primary value after exposure to $(4.5-5.5)\times10^7$
molec cm$^3$ h OH (Table 1), which is expected based on the reaction with OH (Overend and
Paraskevopoulos, 1978) and the low terpene concentrations. Monoterpene concentrations are
below the detection limit in all experiments and isoprene emissions are relatively low (Table 2).
We have previously identified the compounds contributing to the majority of the SOA formed during these experiments (Bruns et al., 2016). The average EF for each of these species is shown in Figure 3. Figure S32 shows the observed decay of the largest SOA precursors contributing the most to SOA formation during aging in the chamber compared to the expected decay based on the OH concentration in the chamber and the reaction rate with respect to OH. There is generally good agreement between the observed and calculated decay for each compound, which supports the structural assignment of each ion. For 2-methoxyphenol and 2,6-dimethoxyphenol (Figure S3 f and i, respectively), the agreement between the observed and calculated decays is not as good as for the other compounds, with slower decays than predicted. This discrepancy may be due to fragmentation of related compounds to form 2-methoxyphenol and 2,6-dimethoxyphenol in the instrument or formation of these compounds in the chamber during oxidation. For o-benzenediol, the decays are initially faster than expected and then become slower with increased aging, possibly due to the presence of isomers with different reaction rates with respect to OH.

3.5 Aged emission variability

As described above, the overall primary emission profiles, as well as total NMOG emission mass emitted, vary considerably for experiments 2 and 3 compared to experiments 1, 4 and 5, with considerably much higher total NMOG emissions in experiments 2 and 3. It is expected that the aged emission profiles also exhibit variability based on the primary emissions. Total acid and O-containing species decrease with aging in experiments 2 and 3, in contrast to experiments 1, 4 and 5, where these classes increase with aging (Figure 4). Formic acid shows the largest increase with aging in all experiments (~190-480 mg kg⁻¹ relative to the primary EF, Figure 5), however, in experiments 1, 4 and 5, this increase contributes much more to the total acid mass as the total acid mass is ~5-15 times lower compared to experiments 2 and 3. An
analogous case occurs for maleic anhydride for the O-containing class of compounds. As formic acid and maleic anhydride are formed from the oxidation of aromatic compounds (Bandow et al., 1985; Sato et al., 2007; Praplan et al., 2014), among others, a higher fraction of aromatic species to the total NMOG emissions will contribute to increases in acid and O-containing NMOGs. Inclusion of NMOGs not quantified by PTR-ToF-MS could impact the trends observed in Figure 6. To determine the impact of the high NMOG emission experiments (2 and 3) compared to the lower NMOG emission experiments (1, 4 and 5) on SOA formation potential, individual SOA precursors with published SOA yields are investigated (Figure 3). The SOA formation potential for each of these 18 compounds is determined as the product of the primary EF and the best estimate SOA yield determined from the literature, as determined previously (Bruns et al., 2016). The total SOA formation potential for each experiment is taken as the sum of the individual SOA formation potentials. Interestingly, the SOA formation potential is similar in all experiments and the average enhancement of SOA formation potential in experiments 2 and 3 compared to the average of experiments 1, 4 and 5 is insignificant (Figure 2), despite the considerably different total NMOG EFs.

4 Conclusions

This study is the first detailed characterization of primary NMOGs from residential wood combustion using a PTR-ToF-MS and the first investigation of the evolution of the majority of these NMOGs with aging. Differences in EFs and profiles between residential burning and open burning can be considerable and these results illustrate the importance of considering these emission sources individually. While total emissions from open burning are much larger than
from residential burning, the societal relevance of residential wood burning emissions is nontrivial. A large fraction of open biomass burning derives from wildfires in sparsely populated regions (Ito and Penner, 2004), whereas residential wood combustion has been shown to be a major fraction of wintertime submicron organic aerosol in densely populated communities (Glasius et al., 2006; Krecl et al., 2008; Gonçalves et al., 2012; Guofeng et al., 2012; Crippa et al., 2013; Herich et al., 2014; Tao et al., 2014; Paraskevopoulou et al., 2015).

Interestingly, MCE does not completely capture inter-burn variability, which is driven by differences in oxygenated content. This work clearly shows that measurements of total NMOGs or total hydrocarbon measurements are insufficient for estimating SOA formation potential from residential wood combustion. While this work characterizes the stable burning of beech wood in a modern woodstove, the composition and quantities of wood combustion emissions are highly dependent on many factors and further work is needed to characterize the emissions and the evolution of these emissions with aging generated from burning of different wood types and under different burn parameters.

Acknowledgements

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Table 1. Modified combustion efficiencies, OH exposures of reported aged values (molec cm\(^{-3}\) h) and enhancement of select species relative to CO enhancement above background levels (pptv ppbv\(^{-1}\))

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<th>parameter</th>
<th>experiment</th>
<th>average(^a)</th>
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<td>0.976±0.002</td>
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<td>OH exposure</td>
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<td>(\Delta CH_3CN_{primary}/\Delta CO)</td>
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<tr>
<td>(\Delta CH_3CN_{aged}/\Delta CO)</td>
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<td>(\Delta CH_3OH_{primary}/\Delta CO)</td>
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<td>(\Delta CH_3OH_{aged}/\Delta CO)</td>
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<td>7±7</td>
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<tr>
<td>(\Delta C_2H_4O_{primary}/\Delta CO)</td>
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<td>30±30</td>
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<tr>
<td>(\Delta C_2H_4O_{aged}/\Delta CO)</td>
<td>12</td>
<td>30±30</td>
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\(^a\)Uncertainties correspond to one sample standard deviation of the replicates.
### Table 2. Primary emission factors of gas-phase species (mg kg⁻¹)ᵃᵇ

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<th>species</th>
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<th>structural assignment</th>
<th>functional group</th>
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<th>4</th>
<th>5</th>
<th>averageᵇ⁻¹</th>
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2- methoxyphenyl)propan-2-one

10H4

11 13 13 11 6.0 11±3

16 31 25 16 8.3 19±9

6.1 3.6 12 15 8.3 9±5

1.4 30 14 3.2 BDL 10±10

2.2 73 35 7.8 1.0 20±30

3.1 BDL 4.3 6.1 2.9 3±2

1.3 0.0 3.2 2.2 1.2 2.2±0.9

2.5 11 6.7 2.2 1.2 5±4

BDL BDL 1.0 2.5 2.0 1±1

0.88 7.6 4.4 1.1 BDL 3±3

BDL 14 6.2 1.1 BDL 4±6

6.4 8.4 6.1 3.6 7.7 6±2

2.7 4.0 2.7 1.2 1.9 2±1

BDL 4.2 2.6 1.1 0.69 2±2

1.1 BDL 1.4 1.1 1.0 0.9±0.5

1.0 7.4 4.2 1.0 BDL 3±3

0.50 2.6 1.3 BDL 0.44 1±1

BDL 1.7 1.2 BDL 0.6±0.8

BDL 0.87 BDL BDL BDL 0.2±0.4

BDL indicates value is below the detection limit.

aCO2, CO and CH4 are measured using cavity ring down spectroscopy and all other species are measured using the PTR-ToF-MS.

bMultiple structural assignments for a given ion correspond to possible isomers.

cUncertainties correspond to one sample standard deviation of the replicates.

dStructural assignment based on known products produced during oxidation of aromatics (Bandow et al., 1985; Chan et al., 2009; Praplan et al., 2014).
Figure 1. Mass spectra of primary emissions for experiments 1-5 (a-e) colored by functional group. (a-e) Labelled peaks correspond to \([C_6H_3O]\) (m/z 43, fragment from higher molecular weight compounds), \([C_6H_3O_2+H]^+\) (m/z 61, acetic acid), \([C_6H_5O_2+H]^+\) (m/z 75, methyl acetate), \([C_6H_5+H]^+\) (m/z 79, benzene), \([C_6H_6O+H]^+\) (m/z 95, phenol) and \([C_{10}H_8+H]^+\) (m/z 129, naphthalene). The bars in (f) correspond to the fractional contribution of each functional group to the total NMOG mass for each experiment and the average of all experiments. Error bars correspond to one sample standard deviation of the replicates. Legend in (b) applies to (a-f).
Figure 2. Enhancement (average value (mg kg\(^{-1}\)) of experiments 2 and 3 relative to the average value of experiments 1, 4 and 5) in each NMOG functional group category and for SOA formation potential. Total SOA formation potential is determined using the primary EF of each NMOG identified as a SOA precursor and literature SOA yields and assumes complete consumption of each NMOG with aging (see text for details). Error bars correspond to one sample standard deviation.
Figure 3. Geometric mean of the primary emission factors for gas-phase species of particular interest for SOA formation (solid bars and gray patterned bars) and identification of air masses influenced by biomass burning (black patterned bars). Colors and patterns corresponding to NMOGs contributing to SOA formation are consistent with Bruns et al. (2016). Error bars correspond to the sample geometric standard deviation of the replicates.
Figure 4. (a-e) Temporal evolution of gas-phase species categorized by functional group throughout aging in the smog chamber for experiments 1-5 (a-e). Units on the y-axes are mass of each functional group (mg) per mass of wood consumed (kg).
Figure 5. Absolute difference of aged and primary mass spectra for experiments 1-5 (a-e), where peaks less than zero decrease during aging and peaks greater than zero increase during aging. Aged emissions correspond to an OH exposure of \((4.5-5.5) \times 10^7\) molec cm\(^{-3}\) h. (a-e) Labelled peaks correspond to \([\text{CH}_2\text{O}_2+\text{H}]^+\) \((m/z\) 47, formic acid), \([\text{C}_2\text{H}_5+\text{H}]^+\) \((m/z\) 61, acetic acid), \([\text{C}_6\text{H}_5+\text{H}]^+\) \((m/z\) 79, benzene), \([\text{C}_6\text{H}_6+\text{H}]^+\) \((m/z\) 95, phenol), \([\text{C}_3\text{H}_4+\text{H}]^+\) \((m/z\) 97, furan-2-carbaldehyde), \([\text{C}_6\text{H}_4+\text{H}]^+\) \((m/z\) 99, maleic anhydride), \([\text{C}_{10}\text{H}_8+\text{H}]^+\) \((m/z\) 129, naphthalene) and \([\text{C}_6\text{H}_4+\text{H}]^+\) \((m/z\) 149, phthalic anhydride). The bars in (f) correspond to the fractional contribution of each category to the total NMOG EF at an OH exposure of \((4.5-5.5) \times 10^7\) molec cm\(^{-3}\) h for each experiment and the average of all experiments. Error bars correspond to one sample standard deviation of the replicates.