

Interactive comment on “Characterization of gas-phase organics using proton transfer reaction time-of-flight mass spectrometry: fresh and aged residential wood combustion emissions” by Emily A. Bruns et al.

Anonymous Referee #1

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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

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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.

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?

In addition to wall loss, I think the authors should also discuss the variability of sec-

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ondary 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 oxygenated 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).

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 O₂ 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.

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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.

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.

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)?

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.

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.

Fig. 4: I assume that each panel is the temporal evolution of gas-phase species from

each aging experiment. Is that correct? Please clarify.

References:

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