Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "OH-chemistry of non-methane organic gases (NMOG) emitted from laboratory and ambient biomass burning smoke: evaluating the influence of furans and oxygenated aromatics on ozone and secondary NMOG formation" *by* Matthew M. Coggon et al.

Anonymous Referee #1

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General comments:

This paper investigates the role of a number of identified furans and other oxygenated aromatic compounds in the chemistry of ageing biomass burning emissions. Chemical schemes are developed for these species, and are used to extend the chemistry in the Master Chemical Mechanism (MCM). The extended mechanism is used to interpret the results of simulation experiments in which biomass burning smoke is oxidized in a

chamber under illumination from UVC lamps; and the description of secondary organic compound formation (measured by PTR-ToF-MS) is reported to be improved. The mechanism is also tested in a Lagrangian box model used previously to model a real biomass burning plume. This is reported to provide an improved representation of the chemistry in biomass plumes, in particular the formation of maleic anhydride which may be used as a tracer for this source.

This is an interesting piece of work, providing results and interpretation that will potentially help to improve the understanding and representation of the chemistry of ageing biomass burning emissions. The work is suitable for publication in ACP, but there are a number of points where additional clarification and information would seem to be required. The authors should address the following comments in producing a revised version of the manuscript.

Specific comments:

Lines 107-115: Some information is given here on primary OH radical sources in the "mini-chamber", and more generally in Sect. 3.2.3 and the SI about photolysis rates using the UVC lamps. MCM v3.3.1 recommends sources of cross-section and quantum yield data in relation to the specific and generic photolysis processes it represents (http://mcm.leeds.ac.uk/MCMv3.3.1/parameters/photolysis.htt). Can the authors confirm that these were used, or provide more details on what information was used (e.g. in Table S1 for emitted compounds and elsewhere for product species, e.g. carbonyls, hydroperoxides and nitrates)?

Line 122. It is stated that "Gas-phase species have a high affinity to metal surfaces. . .." Acetonitrile is a gas phase species, but is assumed not to be lost to surfaces (stated in the SI). Perhaps a little more information on this is required in the manuscript, including a reference to support the acetonitrile assumption.

Line 129: "Deuterated butanol" is abbreviated as "d-butanol". Neither of these terms tells the reader what the molecule actually is, and more clarification is required. In-

deed, the prefix "d-" (as opposed to "l-") usually specifies the rotation direction of optical activity… and this is not relevant in this case. Assuming "deuterated butanol" is the same species for which Barmet et al. (2012) measured the OH rate coefficient (line 139), it is CD3CD2CD2CD2OH. This should be identified as "1-butan-d9-ol" or "butanol-d9".

Line 265: A little more explanation could be provided on the deviations between chamber and ambient chemistry that occur at high OHR, and why values of 70 s-1 and below are acceptable.

Line 390: The use of the MCM a-pinene mechanism alone to represent all monoterpenes seems unnecessarily simplistic. As stated, the MCM includes a-pinene, b-pinene and limonene as examples of monoterpenes respectively containing endocylic-, exocyclic- and endocyclic- + exocyclic- double bonds, and therefore has significant coverage of the list given previously on line 390. An improved approach would surely have been to represent those three monoterpenes explicitly, and use them as mechanistic surrogates for the remaining ones. For example, the OH- and O3- initiation reactions for camphene (containing an exocyclic- double bond) could be included explicitly in the mechanism, but represented to form the corresponding products in the b-pinene scheme (this being the closest structural representative).

It should also be noted that the MCM includes the chemistry of the sesquiterpene, b-caryophyllene. Presumably, sesquiterpenes are also produced from biomass burning?

Line 423: Hydroperoxide photolysis is a slow process in the atmosphere, even if much more rapid with 254 nm illumination in the chamber. What photolysis rates are used? Reaction with OH will almost certainly dominate in the atmosphere. Have you investigated the effect of assuming a radical forming process (photolysis) in place of a radical propagating process (OH reaction) in the ambient plume simulations?

It would be a very helpful service to the community if the added chemistry was also provided in the form of a reaction listing that can be used in conjunction with MCM

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v3.3.1. It should also be made clear that expressions like "the updated MCM" used at various points in the manuscript do not imply that the MCM itself has been updated. Perhaps "the extended MCM" or "the customized MCM" would be more appropriate.

Line 425: kRO2HO2 actually has a size-dependence term in the MCM, based on carbon number (see Saunders et al., 2003). The quoted rate constant is the limiting value at high carbon number. Was this taken into account?

Line 427: Although MCM v3.3.1 does not generally contain RO2 H-shift isomerization reactions, it does contain those specifically identified to occur during the degradation of isoprene (see Jenkin et al., 2015), which is included in the speciation applied in this study. Perhaps this statement should be qualified accordingly.

Line 457: If butanol-d9 is a significant contributor to OH reactivity, this approach would seem over simplified. Fig. 7 suggests use of 45 ppb, equating to and OH reactivity of about 3.8 s-1 - compared with about 2.3 s-1 for 5-methylfurfural and 2-methylfuran collectively. If this latter pair is significant (as stated on line 399) then butanol-d9 is even more significant and it would seem prudent to represent its chemistry more explicitly.

There is also the possibility that its degradation might form products of masses that interfere with those from the studied oxygenated compounds, and this should be checked. Based on a quick appraisal, I think one product type (C4H2D8O3 - i.e. CD3CD2CD(OOH)CD2OH and CD3CD(OOH)CD2CD2OH) is formed in the first generation of oxidation of butanol-d9, from RO2 + HO2 reactions. This has an interfering mass of interest (114), which I believe is isobaric with methyl hydroxy furanone and beta-acetylacrylic acid.

Line 498: Presumably, the slower decay might also result from formation of isobaric products in the system?

Line 528: Statements like "....chemical pathways that are unaccounted for within MCM v 3.3.1" are very easy to include as explanations, but are often not backed up by evi-

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dence or specific examples. The degradation of almost all VOCs produces formaldehyde, and this is actually generally found to be substantial and quite well represented in MCM. For example, looking at your list of species, the 3 most abundant (after formaldehyde itself) are 1-butene, methanol and ethene, with these making a collectively significant contribution to the OH reactivity. 1-butene and methanol generate formaldehyde essentially quantitatively (on a molar basis) from radical propagation pathways in the first oxidation step, with ethene producing about 1.7 molecules of formaldehyde. MCM represents this very well, and continues to represent formaldehyde formation from the further oxidation of C2 and higher products (e.g. C2H5CHO from 1-butene). Going on down the list, most of the species make formaldehyde from first- and/or higher-generation chemistry in MCM v3.3.1 - but with the obvious exceptions being species that do not contain a -CH2- substructure (e.g. ethyne, formic acid, glyoxal, phenol and benzene) which cannot make formaldehyde. The much more likely explanation for the under-representation of formaldehyde formation is therefore missing species in the starting speciation. It might also be very sensitive to uncertainties in the [NO] initialization in the model, as this would influence the relative importance of radical propagation and radical termination processes.

Line 603: MCM only includes RO2 + NO2 for acyl peroxy radicals and CH3O2. The reaction is not represented in most cases because the RO2NO2 products are thermally unstable and rapidly regenerate RO2 and NO2 (as indeed the CH3O2 + NO2 reaction does at 298 K). The RO2 + NO2 contribution is therefore probably dominated by a very limited set of reactions. The C1 reaction is only CH3O2+NO2, C2 is probably dominated by CH3C(O)O2 + NO2, C3 by C2H5C(O)O2 + NO2: and the small C7 contribution is probably mainly C6H5C(O)O2 + NO2. Figure 9 therefore suggests that this limited set of reactions has a big effect. It might also be more correct to check the back decomposition rates for RO2NO2 = RO2 + NO2 and to present the net (forward minus reverse) effect of the RO2 + NO2 reaction - particularly for CH3O2 + NO2 = CH3O2NO2. Note also that the decomposition rates are very sensitive to temperature. Was temperature measured in the mini-chamber and taken into account in the

simulations?

Typos:

Line 399: "2-dimethylfuran" should be either "2-methylfuran" or "2,5-dimethylfuran".

Line 586: "undesireable" should be "undesirable"