

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. Coggan et al.

Anonymous Referee #2

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Coggan et al., have used an extensive data set of PTR-ToF-MS and I-CIMS measurements, carried out during a wide range of chamber biomass burning /OH oxidation experiments in order to investigate the impact of a range of observed emitted furans and oxygenated aromatics on the formation of secondary reactive VOC and ozone in aged smoke. This was inferred from model/measurement comparisons of detailed chemical box modelling, where schemes from the Master Chemical Mechanism (MCMv3.3.1) were updated and extended. The results highlight significant formation of a range

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of C4 and C5 anhydrides and furanone species in aged biomass burning plumes. The derived mechanisms were put into a Lagrangian box model in order to model the chemical evolution of a real life biomass burning again highlighted the importance of furan chemistry and its impact on ozone formation.

The work presented is scientifically and mechanistically interesting and the comprehensive compositional measurement dataset, mechanism development and model interpretation work significantly adds to our further understanding of the atmospheric impact of biomass burning on fundamental atmospheric chemistry and air quality. The work is very much suitable for publication in ACP, after the following comments and clarifications have been addressed.

Specific points

“mini-chamber” experiments and the use of UVC lamps as a large, “clean” source of OH

The burn smoke is diluted with humidified air (why 30%?) and introduced into the mini-chamber along with ozone (why 70 ppb?), where the chamber reactive mixture is exposed to (predominantly?) 254 nm UVC radiation in order to produce OH to initiate the chemical degradation of the chamber mix. Therefore, the chemistry in the system is not carried out under atmospherically relevant conditions, these studies are aimed mainly at looking at the mechanisms of the OH chemistry. The chemistry is dominated by OH chemistry, with little information given on the NOx and NOy composition in the mini-chamber (only estimated from stack measurements) and any photolysis chemistry of photo-labile species is occurring at non-atmospherically relevant wavelengths.

There is little information given on the chamber auxiliary chemistry mechanism needed in order to the background reactivity of the chamber in the chamber specific box modelling. For example, processes that need to be taken into account include: introduction of free radicals from heterogeneous chamber wall reactions; adsorption/desorption of NOy species (including HONO) to/from the chamber walls; off-gassing of various re-

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active species from the chamber walls, which can contribute significantly to the radical budget of the system. Also, initial HONO concentration is important to know. Is a detailed chamber auxiliary mechanism available and used here? Formic and acetic acid are shown to be significant secondary product VOCs in the experiments (Line 288). These small oxygenates, as well as HCHO and HONO have significant wall sources in Teflon chambers. Have these sources been taken into account? (in the chamber auxiliary mechanism).

It is stated at line 238/239 that “radical reactions and NOx loss process are likely sensitive to initial NO/NO₂ ratios”, have any model sensitivity analyses been done to look at this sensitivity?

More chamber details are needed – mixing time, spectrum of the lamp used and how was the photon flux derived; how uniform throughout the chamber is the photon flux exposure?

As the other reviewer points out, information on the photolysis rates of some of the primary photo-labile VOCs, along with rate constants for other atmospherically important oxidants are given in the SI. However, little to no information has been given as to the sources of these important data are given. Also, how were the photolysis rates calculated? It is important to note that the MCM chemical mechanisms are designed for use in tropospheric chemistry models, where the cross-sections and quantum yield data used to derive the photolysis rates are mainly used at > 290 nm. Therefore, any primary and secondary MCM chemistry used here in the chamber modelling (but not in the BB plume models) needs to be adjusted to photolysis < 290 nm (mainly around 254 nm). For example, the 1,4-dicarbonyl chemistry (mainly 2-butenedial and 4-oxo-2-pentenal, which are significant products from the atmospheric chemistry of aromatics and furans) in the MCM is mainly driven by photolysis (see Newland et al., 2019), where the main photolysis products are furanones and maleic anhydride (a main focus of this study). However, at 254 nm, the photolysis product distribution (quantum yields and photo-tautomer distributions) are different (Tang and Zhu 2005).

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I agree with the other referee that given that a) monoterpenes contribute significantly to the calculated OH reactivity on the experiments and b) the MCM contains extensive chemical mechanism for the atmospheric degradation of both alpha and beta pinene, as well as limonene (and beta caryophellene), using a-pinene as a proxy is an oversimplification here (Line 394).

Line 80 – define “0-D” Line 105 – define “semi-batch” Line 275 – why is an OH atmospheric concentration of 1.5E+6 cm⁻³ assumed? Line 353 – “I-ToF-MS” should be I-CIMS? Line 364 – “anthropogenic and biogenic aliphatic and aromatic species” Line 484 – reference needed for the o-semiquinone chemistry Line 501 – is this exhibiting a “bi-exponential” decay profile? Line 515 – could the model be underpredicting the MA yield owing to increased MA and furanone yields from 1,4-dicarbonyl photolysis at 254 nm? Line 537 and Figure 2 – under-prediction of small oxygenates – some of this could be coming from wall sources? (e.g. Zador et al., 2005) Line 560 – ozonolysis of other monoterpenes than a-pinene could be more important? Line 718 – “understudied NMOG OH chemistry” – this study really focuses on the OH chemistry Line 721 – what does “understory” mean?

Figure S6, S7 and S9 – J<41> (CH₃OOH photolysis rate) – has this been adapted for 254 nm photolysis? Figure S10 – what is GUAIACOLPROD? Figure S14 – give structure of HYDMEFURANO2 on plot

M. Newland et al., Phys.Chem.Chem.Phys., 2019, 21, 1160. Y. Tang and L. Zhu, Chem. Phys. Lett., 2005, 409, 151–156. Zador, J., Turanyi, T., Wirtz, K., and Pilling M. J. J. Atmos. Chem. 55, 147–166, 2006.

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