

### **General comments:**

Bogler et al. present an insightful study on the ozonolysis of biomass burning organic aerosols (BBOA) using flow reaction systems coupled with advanced mass spectrometry analysis. The manuscript thoroughly examines the chemical evolution of BBOA under varying relative humidity and ozone exposure conditions, offering a well-supported mechanistic discussion. This research addresses an important topic related to the atmospheric fate of wildfire and prescribed burning emissions, which play a crucial role in the atmosphere-climate system. The manuscript is well-structured, clearly written, and includes a detailed discussion of the results. Therefore, I believe it is well-suited for publication in *Atmospheric Chemistry and Physics* following minor revisions. Below, I provide a few specific comments that the authors may find helpful in further strengthening their study.

### **Specific comments:**

Line 50: It may be worth noting that sunlight can also drive triplet-state chemistry and secondary oxidant formation inside BBOA particles, contributing to oxidative processes (Liang et al. 2024). Additionally, recent fieldwork by Vasilakopoulou et al. (2023) reported the rapid oxidation of biomass burning plumes, which could provide further context.

Line 75: Given the discussion on O<sub>3</sub> diffusion limitations in BBOA, it would be beneficial to elaborate on how liquid-liquid phase separation (LLPS) can lead to the formation of a highly viscous shell, which may further restrict oxidant penetration (Gerrebos et al. 2024; Gregson et al. 2023).

Line 80: It would be helpful to provide additional context on the prevalence of these fuel types in ambient environments, particularly in wildfire-prone regions, to strengthen the relevance of the study.

Line 100: Since combustion conditions significantly influence BBOA composition, mentioning the typical burning temperatures in real wildfire and prescribed burn scenarios would enhance the discussion.

Line 108: Is AADCO XX the brand of the gas generator?

Line 160: A discussion on how the low solubility of certain BBOA components might affect the performance and sensitivity of the EESI-ToF analysis would be valuable.

Line 240: It would be interesting to see whether the DBE plot captures the depletion of high DBE compounds upon oxidation, which could further support the loss of reactive species.

Line 248: Knopf, Forrester, and Slade (2011) reported ozone uptake by LEVO particles, though the detailed chemical mechanism remains unclear. A brief mention of this could provide additional context.

Line 282: The statement on volatility changes upon oxidation could be further elaborated, as increased volatility is often expected but depends on the specific reaction pathways involved.

Line 299: Were any aromatic compounds with vinyl side chains, such as coniferyl alcohol, detected? These species are commonly found in BBOA and are known to undergo ozonolysis (Fleming et al. 2020; Huang et al. 2021).

Line 322: Gregson et al. (2023) suggested that the BBOA can undergo LLPS to form a highly-viscous shell.

Line 344: Did the author refer to 'mass accommodation' and 'bulk phase diffusion to reach mass equilibrium'?

Line 391: The discussion on interfacial processes could be expanded, as the interfacial layer (~0.15 nm thick) in a 100 nm particle would only account for approximately 1% of the total particle volume. A quantitative perspective on this aspect would be helpful.

Line 400: The discussion on phase state as a key factor in multiphase oxidation is highly relevant. However, it would be useful to briefly comment on the oxidation of BBOA by other oxidants, such as OH radicals. Since BBOA has limited reactivity toward ozone due to a lack of unsaturated moieties, OH radicals may play a more significant role by abstracting hydrogen from a wide range of organic species. Additionally, internal oxidant production via photosensitization—beyond multiphase uptake—could be worth mentioning, as it does not require gas-to-particle diffusion and may be particularly relevant under dry or cold conditions.

I appreciate the authors' efforts and look forward to seeing this work published in *Atmospheric Chemistry and Physics*!

## Reference

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Huang, Ru-Jin, Lu Yang, Jincan Shen, Wei Yuan, Yuquan Gong, Haiyan Ni, Jing Duan, Jin Yan, Huabin Huang, and Qihua You. 2021. 'Chromophoric fingerprinting of brown carbon from residential biomass burning', *Environmental Science & Technology Letters*, 9: 102-11.

Knopf, Daniel A, Seanna M Forrester, and Jonathan H Slade. 2011. 'Heterogeneous oxidation kinetics of organic biomass burning aerosol surrogates by O<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub>, and NO<sub>3</sub>', *Physical Chemistry Chemical Physics*, 13: 21050-62.

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Vasilakopoulou, Christina N, Angeliki Matrali, Ksakousti Skyllakou, Maria Georgopoulou, Andreas Aktypis, Kalliopi Florou, Christos Kaltsonoudis, Evangelia Siouti, Evangelia Kostenidou, and Agata Błaziak. 2023. 'Rapid transformation of wildfire emissions to harmful background aerosol', *Npj Climate And Atmospheric Science*, 6: 218.