

Comment on acp-2022-312

Anonymous Referee #1

Referee comment on "The influence of the addition of isoprene on the volatility of particles formed from the photo-oxidation of anthropogenic–biogenic mixtures" by Aristeidis Voliotis et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-312-RC2>, 2022

SOA is important to both air quality and climate. Most previous studies predicted the SOA mass based on the SOA yield method from a signal precursor. However, VOCs and their oxidation products in the real atmosphere are a complex mixture (Nie et al., 2022). The interactions among different VOC oxidation processes can potentially influence the SOA yield but are largely understudied. This study investigated the influence of isoprene on the SOA formation from α -pinene, *o*-cresol, and their mixtures. The results did provide useful information and fit the scope of ACP. However, I have a few comments before this manuscript can be published.

- **Reliability of measurement technology:** Thermal denuder and FIGAERO-CIMS need to heat the sample before detection. This may induce interferences via thermal decomposition, as well as chemical reactions occurred during the heating. For example, in the α -pinene/isoprene mixture system, there were no detected product molecules with $nC=15$ (Fig. 4a), which should be one crucial group of products from the cross-reactions between C_{10} -RO₂ and C_5 -RO₂. In addition, most detected molecules by FIGAERO-CIMS were less oxidized (lower O:C) than those observed in the gas phase. What's the possible reason? And how to evaluate these possible instrument-induced interferences?
- **Calculation method of partitioning coefficient (Line 230):** This method is only valid when a compound is in equilibrium between the gas and particle phases and cannot be used to assess the volatility of very condensable compounds ($< LVOC$). Moreover, considering the large number of potential gas- and particle-phase reactions, it is difficult to ensure that compounds with the same molecular formula in both phases are indeed the same molecule, i.e., have the same molecular structure. The authors need to provide more results to clarify the accuracy, uncertainty and applicability of the method. Given the use of FIGAERO-CIMS, the authors may be able to infer volatility based on thermograms for individual molecular components (Thornton et al., 2020), and may be able to obtain information by comparing the results of the thermal-desorption-based approach with the results of the equilibrium method used in the text.
- FIGAERO-CIMS can also measure the gas-phase oxidation products. Why not add some discussions of gas-phase chemistry to support the interpretation of the aerosol phase observation?

- **To Line 298-300:** The carbon number is not shown in Fig. 1c and Fig. S1.
- Table 1: Exp. 1-4: why the SOA yield change from 0.32 to 0.15?
- **To Line 357, 380, 408-409:** Based on the assigned elemental formulas, many compounds seem to be not closed-shell molecules, e.g. $C_{10}H_{10}NO_4$ and $C_{12}H_{11}O_4$, etc. Can the authors supply the results of HR peak fitting (including the measured signal, the fitted peak and the residual)?
- **To Line 449-450:** It seems that SOA particle mass yield of o-cresol was reduced by the presence of isoprene (from 0.11 to 0.06/0.05).
- **To Line 541:** As shown in the study of McFiggans et al. (2019) and Heinritzi et al. (2020), isoprene depletes OH radicals, preventing their reaction with monoterpenes, and the resulting isoprene peroxy radicals scavenge highly oxygenated monoterpene products. These effects ultimately suppress both particle number and mass of secondary organic aerosol. It can be simply inferred that the mass yield, composition, and volatility of SOA will be altered after mixing isoprene in the monoterpene system, but this was not the case in this study. Given that FIGAERO-CIMS can provide near-molecular information, it is appropriate for the authors to discuss the above situation.

Reference

Nie, W., et al., Secondary organic aerosol formed by condensing anthropogenic vapours over China's megacities. *Nature Geoscience*, 10.1038/s41561-022-00922-5, 2022.

Heinritzi, M., et al., Molecular understanding of the suppression of new-particle formation by isoprene, *Atmos. Chem. Phys.*, 20, 11809-11821, 10.5194/acp-20-11809-2020, 2020.

McFiggans, G., et al., Secondary organic aerosol reduced by mixture of atmospheric vapours, *Nature*, 565, 587-593, 10.1038/s41586-018-0871-y, 2019.

Thornton, J. A., et al., Evaluating Organic Aerosol Sources and Evolution with a Combined Molecular Composition and Volatility Framework Using the Filter Inlet for Gases and Aerosols (FIGAERO), *Accounts of Chemical Research*, 53, 1415-1426, 10.1021/acs.accounts.0c00259, 2020.