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Interactive comment on "Halogenation processes of secondary organic aerosol and implications on halogen release mechanisms" *by* J. Ofner et al.

Anonymous Referee #1

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This manuscript reports an extensive analysis of secondary organic aerosols (SOA) following exposure to reactive halogen species, namely Cl and Br generated either through the photolysis of Cl2 or Br2, or from simulated "salt pans" (i.e., wet NaCl/NaBr surface exposed to O3). The study directly compared results for SOA produced from α-pinene, catechol, and guciacol, noting differences from halogenation reactions depending on the organic precursor. SOA characterization, measured both before and after halogenation, included: mean particle diameter; differential UV-visible absorbance; ATR-FTIR; and high resolution mass spectroscopy, which produced H/C ratio van-Krevelen diagrams and estimated carbon oxidation states. The results provide clear evidence for heterogeneous halogenation of all precursor-type SOA, which should be of great interest to the readers of ACP given the potential impact of such chemistry in the atmosphere, especially in the marine boundary layer and over salt pans. Given the thoroughness of the characterization described within, the most significant void, in my opinion, is the lack of specific chemical reactions/mechanisms explaining these observations. Admittedly, many of the results hint at very complex chemistry, nonetheless I would encourage the authors to share their thoughts and insights regarding potential reactions to begin building a framework for understanding this chemistry (e.g., The concomitant loss of carboxylic acid functional groups with the appearance of C-Cl vibrations). There are also a few areas, discussed below, where further clarification and/or revisions would enhance the discussion of this manuscript.

- 3.1 Change of aerosol size-distribution: Formation of a second aerosol size mode for guaiacol SOA upon introduction of molecular chlorine stands out in contrast to all other organic precursors. Did the authors study potential SOA formation for guaiacol + Cl2 + hν in the absence of O3? Is hydrogen atom abstraction from the methyloxide group of guaiacol responsible for the distinctive chemistry resulting in the second mode of particles? This interesting result deserves an expanded discussion in the paper.

- 3.2 Optical properties in the UV/VIS range: The presentation of differential UV-visible absorption demonstrates changes in particle optical properties, but it is difficult to appreciate the significance of these modifications. Further clarification on the extent of change relative to the initial absorption properties would be helpful. Perhaps including the total absorbance measurements in addition to the differential spectra would most effectively present this data. Given the normalization coefficients used in generating the difference absorption plots, equation (1) is not rigorously correct. Please include these normalization coefficients in eq (1) to accurate reflect the calculation of dA.

- 3.3 Changes in vibrational features of gaseous species: Readers would be aided if the authors explicitly states that “positive peaks correspond to decreasing species while negative peaks are associated with increasing species.” This is reverse what I typically expect and might ask the authors if they considered showing absorbance differences rather than percent transmittance differences. Related to this is the potential to quantify the amounts of gaseous species since the cross-sections for each of the identified species are well known (e.g., PNNL Northwest-Infrared library). This would aid the reader in appreciating the significance of these observations more so than the qualitative “weak” vs “strong” notation in Table 1. For instance, is there a one-to-one relationship between CO lost and phosgene formed for catechol SOA exposed to chlorine?

- 3.3 Changes in vibrational features of ... particulate matter: Figure 5 already has a lot of data, but it would be preferred to also include the ATR-FTIR spectra of unprocessed SOA to provide the reader a direct visual comparison of the chemical changes. I would encourage to authors to consider revising this figure to include such spectra.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2975, 2012.