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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Phase partitioning and volatility of secondary organic aerosol components formed from alpha;-pinene ozonolysis and OH oxidation: the importance of accretion products and other low volatility compounds" *by* F. D. Lopez-Hilfiker et al.

Anonymous Referee #3

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General comments:

This manuscript discusses and interprets measurements from a Filter Inlet for Gases and AEROsols (FIGAERO) coupled to a High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS). Measurements were taken of gas and particle-phase species formed during ozonolysis and OH oxidation of alpha-pinene in a glass chamber and a Teflon chamber. The FIGAERO HR-ToF-CIMS is capable of measuring gas and particle-phase species – gas species are measured when bypassing the FIGAERO, and particle-phase species are measured by first collecting particles on a filter and then slowly heating the filter and measuring the vaporized species. The acetate ion was used for chemical ionization which is primarily sensitive to organic acids and similar species. Particulate matter concentrations were also measured using an aerosol mass spectrometer, and total organic aerosol mass loadings were compared to the measurements form the FIGAERO HR-ToF-CIMS. Desorption profiles (signal versus filter temperature) were used to estimate species' vapor pressure, and the authors conclude that 50% or more of the organic aerosol has saturation mass concentrations below 10ˆ-5 micrograms/mˆ3, implying that fraction should be treated as effectively nonvolatile.

The FIGAERO HR-ToF-CIMS allows for semi-continuous analysis of gas and particle-phase species and as such presents a significant asset to the research community's measurement capabilities. This is, to the best of my knowledge, the first manuscript quantifying organic particulate matter volatility from FIGAERO HR-ToF-CIMS data, and it is hence of great interest to the research community. The manuscript is well written and should be published in ACP after all reviewers' comments have been addressed. I have a few concerns about quantification of organic species as detailed below.

Specific comment 1:

Considering that the authors compare particle-phase measurements from the FIGAERO HR-ToF-CIMS to organic aerosol measurements from the AMS, the AMS data collection and analysis should be described in more detail. AMS measurements and data analysis are subject to significant uncertainty, for example due to particle bounce at the vaporizer resulting in a non-unity collection efficiency, which could even change over the course this experiment as the ratio of inorganic seed aerosol to organic aerosol changes.

Specific comment 2:

In order to quantify FIGAERO HR-ToF-CIMS species concentrations the author use the instrument's sensitivity to formic acid and apply that sensitivity factor to all measured species (hundreds of species). They argue that "this assumption is reasonable within a factor of 1.5" based on calibration data shown in Fig. 1. I am not convinced for several reasons:

a) The sensitivity factors in Fig. 1 seem to span 2 orders of magnitude, so it is not clear to me why this assumption is thought to be reasonable within a factor of 1.5

b) The sensitivity factors in Fig. 1 are for carboxylic acids only. As the authors note the FIGAERO HR-ToF-CIMS with the acetate reagent ion is sensitive to all "acyl compounds" which includes but is not limited to carboxylic acids. Thus, it seems appropriate to also measure sensitivity of the instrument to non-acid compounds and compare to the sensitivity of the acids before determining / estimating a general sensitivity factor.

Specific comment 3:

Based on analysis of the desorption profiles the authors conclude that at least 50% of the SOA is due to essentially non-volatile species (very low C*). I am concerned about this quantitative measure considering that a single sensitivity factor was applied to all measured species. This result will be biased if species of different vapor pressure have different sensitivities in the FIGAERO HR-ToF-CIMS. Has this been investigated (sensitivity to a compound vs. the compound's C*)? The authors conclude that much of the low-volatility compounds can be attributed to accretion products (e.g. oligomers). Have there been measurements of the sensitivity of the FIGAERO HR-ToF-CIMS to an oligomer and its corresponding monomer? Would one expect the oligomer and monomer sensitivity to be similar? Finally, if after consideration of my comments the authors still conclude that their data suggest that over 50% of the SOA is essentially non-volatile, it would be appropriate to comment on the implication of such a result to the larger research community, e.g. how would might affect organic aerosol modeling efforts.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 4463, 2015.