

Interactive comment on “Quantitative estimates of the volatility of ambient organic aerosol” by C. D. Cappa and J. L. Jimenez

Anonymous Referee #1

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Review of ‘Quantitative estimates of the volatility of ambient organic aerosol’

The general findings of the paper are very interesting, specifically the large portion of OA prescribed as non-volatile. The majority of the paper is well written and the research is both timely and highly significant. I only have some general comments to make and one specific point.

Some general comments

In the introduction it would be good to present the reader with a brief overview of attempts used to derive what one would call mechanistic frameworks using bottom-up approaches. Whilst not as easily or directly applicable to, let's say, large scale prognostic models, these approaches are attempting to attack the problem from a completely

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different yet entirely complimentary angle. Whilst a thorough review is clearly outside of the present scope of the paper, the use of adequate references alluding to these approaches would help place the current work within a wider framework.

Section 2.

Page 1906-1907. In the discussion of enthalpies of vaporization and impacts of variations in C^* , the authors reference studies on individual dicarboxylic acids. Would the authors consider these acids as adequate ‘reference’ points from which to generalise results? Again, I understand the difficulty here, but it is likely that many readers do not given the relative infancy of this area with regards to atmospheric science.

Section 3.1

Results presented here are important in understanding the difficulties in reproducing appropriate volatility distributions. The text however is rather difficult to follow in places and I personally had to keep double checking results in places. I appreciate the discussion of quite detailed results is hard, but it may help the reader to present a series of bullet points summarizing the constraints which enabled reconciliation between model/measurements before a general discussion.

One specific point:

On page 1914 the authors make the statement that:

‘For example, the addition of a single ketone function group to a straight-chain hydrocarbon decreases the vapor pressure by approximately a factor of 10, the addition of an alcohol group by a factor of 100 and the addition of a carboxylic acid group by a factor of 1000 (c.f. Fig. 1b in Goldstein and Galbally, 2007).’ This statement is a bit sweeping. The context in which the authors are using this rule of thumb would suggest that as it doesn't refer to multifunctional compounds. Providing it is clear that the factors of 10, 100 and 1000 are very approximate then the statement is OK. However, whilst it may be true for straight chain hydrocarbons, it is risky to extrapolate this behaviour

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to multifunctionals. Chattopadhyay and Ziemann (2005) see extra alpha hydroxy groups raising the vapour pressure. Results from Knudsen effusion also show perhaps unexpected behaviour with extra OH groups and single ketone groups with regards to the subcooled vapour pressure, which is raised rather than lowered by extra groups. This is probably due to intramolecular bonding.

Conclusions. The overview of findings presented in this study is great. Using variations of the volatility basis set as a relatively detailed diagnostic tool is interesting and should be included in future studies. It would be good if the authors could comment on the general applicability of this approach in future field campaigns and what limitations there may be dependent on the environment studied...if this is possible to predict?

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 1901, 2010.