Review of “Solid state and sub-cooled liquid vapour pressures of cyclic aliphatic dicarboxylic acids” by Booth et al.

Development of predictive, empirical relationships between molecular structure and temperature-dependent vapor pressures remains an important task, as such predictive relationships are used to determine vapor pressures for compounds within models of SOA formation. However, the utility of such measurements is hampered somewhat by the lack of data for very “low” volatility compounds and for multi-functional “low” volatility compounds (i.e. the empirical paramaterizations are typically developed using compounds with vapor pressures well above the range of interest for atmospheric applications). In this manuscript, Booth et al. expand the database for vapor pressures of low-volatility compounds by focusing on cyclic aliphatic dicarboxylic acids. This study allows for the assessment of how structure affects vapor pressures, since the authors have previously determined T-dependent vapor pressures for other dicarboxylic acids with the same carbon number but different structures (e.g. linear).

Overall, the measurements appear to be of high quality. However, I find the discussion to be generally lacking in thoroughness. For example, literature data is presented that is never discussed in the manuscript (e.g. azelaic acid or the branched C7 diacids). Also, the authors focus their discussion on vapor pressures only, but they have also measured enthalpies of vaporization, which are just as important as vapor pressures. Some discussion of the enthalpies of vaporization, and in particular how they differ between linear and branched structures, should be provided. For example, are there any relationships between how ΔH_{sub} changes from linear to cyclic and how the VP changes from linear to cyclic? Can the authors suggest a reason that the ΔH_{sub} for 1,1-cyclopropane dicarboxylic acid is so much larger than for the other cyclic diacids considered here? For the linear diacids, ΔH_{vap} generally increases with increasing carbon number (after accounting for the odd-even behavior), but here the opposite is observed. For the cyclic C7 diacid, the vapor pressure is essentially the same as for the linear variant, but the observed ΔH_{sub} is much, much lower (66 vs. 147 kJ/mol). This seems to me to be worth commenting on as it is a somewhat surprising result. However, this is just one example of how the discussion could be expanded to make the discussion more complete. Once the overall discussion is flushed out further, I think that the manuscript will be publishable. Specific comments/suggestions follow below.

General Notes:

P. 23018-23019: The lengthy discussion of different VOC emissions seems somewhat out of place and distracts early on from the focus of the manuscript. The authors could much more succinctly get across their point that there are a vast number of potential SOA forming compounds in the atmosphere that come from myriad sources.

P. 23021, L. 13: The reference to Booth, 2010 would better be to one or more of the papers that actually develop the estimation methods.

Section 2.2: The discussion of the “slope” makes it seem as if there is a linear relationship between temperature and vapor pressure, which is not the case. The authors should make clearer how this

temperature-adjustment is done. I assume it is some sort of Clausius-Clapeyron type equation. Also, an equation in this section might be useful. For example, the very last sentence mentions how ΔS_{vap} is calculated, but it is not made clear in the discussion why ΔS_{vap} how it is specifically used.

Section 3: I suggest adding two sub-headings, one for KEMS and one for DSC, to break up the discussion.

Table 2: Could probably put this in supplementary material, but up to the authors.

Table 3: Caption should indicate clearly somehow that this is not *all* literature observations, but only a selected subset of measurements made using particular techniques.

Table 3: For 2,2-dimethyl glutaric acid it is not clear how the values were "extrapolated to 298 K" if ΔH_{vap} is not known. This should be given if it is, and if not it should be made clear how the extrapolation was done.

P. 23024, L. 23: It is understandable why the authors choose to use the similar Knudsen mass loss results for comparison purposes, but it is not made clear why the TDMA values are used instead of any of the other methods that were discussed in the introduction, at least for compounds where VP's derived from multiple techniques exist. This certainly should be made clear, and *justified* given that the various measurement techniques do not necessarily all agree. Also, the comma after "loss" should be a semi-colon and references given for the TDMA measurements.

Figure 3: I recommend the authors use color within the figure to help visually distinguish between the measurements made using different techniques. The +, -, x's work to some extent, but I think color would make the picture a lot clearer.

Section 4.1.2: The authors state that "1,1 cyclobutane, adipic, 2-methyl glutaric and 3-methyl glutaric, show the same solid state vapour pressure for the cyclic and branched, but the straight chain results are lower by two orders of magnitude." Then, later they state "The sub-cooled liquid vapour pressures, compared to the C6 cyclic compounds show 20 a ~3 fold reduction for the straight chain and a 1.5 factor increase for the branched." However, if one looks at the figure, the difference between the cyclic and branched between solid and liquid particles is effectively identical. Therefore, it does not seem fair or consistent to say that in one case they "show the same" vapor pressures but in the other they show a "1.5 factor increase." The discussion should be adjusted to be self-consistent.

Section 4.1.3: No discussion is given regarding the VP's of the other branched (as opposed to linear and cyclic) C7 diacids. Either some discussion should be added or they should be removed from Figure 3. In other words, why present them if they are not going to be discussed? Similarly, there seems to be no reason to include values for azelaic acid (the linear C9 diacid) in the tables or figures. For one, no discussion is given regarding this compound and also the focus of this paper is on the cyclic diacids and no measurements are presented for a cyclic C9 diacid. So the inclusion of the C9 diacid seems completely out of place (unless, or course, the authors wish to provide some context).

Section 4.1.4: The statement "The lower solid state vapour pressure for 1,2 cyclopentane dicarboxylic acid may be explained simply by that compound having a more stable crystal structure" is ambiguous.

Lower than what? And I thought that the authors just got done arguing that crystal structure effects are not important for the cyclic diacids. Whether they are or are not, there is a lack of self-consistency in the discussion.

Table 7: The authors should include in this table the ratio between the measured and modeled (or the inverse) to facilitate easy comparison. This value could be placed, for example, in parentheses after the vapor pressure. In fact, I would argue that the ratio is the more important parameter in the context of this manuscript than the absolute vapor pressure and thus, if anything, the table could be filled with the ratio model/measurement ratio rather than the model VP's.

Table 7: Presumably, the models also predict ΔH_{vap} in order to allow for movement from the boiling point to 298 K. A comparison between measured and calculated ΔH_{vap} would be useful.

Levoglucosan: The authors comment that the Moller method is the most inaccurate, being 3 orders of magnitude off of the measured values. But really, the more important aspect seems to me to be that all methods are off by 1-2 orders of magnitude, i.e. they are all bad!

Tables 4 & 5: It could be interesting to add a column that gives the ratio between the sub-cooled and solid vapor pressures, for easy comparison.

General: It could be interesting to have a more complete discussion of measurement accuracy vs. precision. The authors calibrate their KEMS system using a particular compound, but if one considers values for malonic acid vapor pressures in the literature it is clear that reported values range over an order of magnitude, much larger than the +/- 40% stated as the maximum error. Certainly, this value must be a measure of the precision of the measurement, and not the absolute accuracy, since the accuracy can only be as good as the calibration compound used. Noting that the KEMS measurements for malonic acid vapor pressures are on the "high" side of the literature values, this suggests then that the KEMS may (and I emphasize may, as opposed to does) have a bias in a particular direction simply because of the calibration compound used. It's certainly possible that the KEMS measurements are the most correct (with biases in the other measurement techniques), but this is (unfortunately) not known at this point. I only bring this up because this has implications for the comparison with the theoretical VP values. Just something to consider.