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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Uncertain Henry's Law Constants Compromise Equilibrium Partitioning Calculations of Atmospheric Oxidation Products" *by* Chen Wang et al.

Anonymous Referee #1

Received and published: 23 March 2017

Reviewer comments: acp-2017-92, "Uncertain Henry's Law Constants Compromise Equilibrium Partitioning Calculations of Atmospheric Oxidation Products"

This manuscript addresses and explores uncertainty in parameters for modeling phase partitioning of atmospheric organic compounds, a critical outstanding source of uncertainty in current atmospheric chemical models. The authors calculate partitioning coefficients between the vapor phase and both aqueous and organic condensed phases using three different approaches built on different underlying methodologies. Discrepancies between these parameter estimation techniques are discussed and used to identify current critical gaps in understanding. In addition, the results of each approach are explored in the context of ambient conditions, and the authors demonstrate that

differences between approaches significantly change the expected phase of many organic compounds in the atmosphere. This work is generally a valuable step toward understanding and eventually addressing current shortcomings in atmospheric partitioning models, and this reviewer recommends publication with only minor revisions.

General comments: 1) By providing the calculated results for all species, this work signficantly advances future modeling. The Excel spreadsheet seems to be corrupt, though, or at least did not work on my computer. Please fix this, and perhaps provide the data in a more portable form as well, such as CSV.

2) Additional detail about the three estimation approaches, in particular SPARC and ppLFER, should be provided in the methods. Throughout the manuscript the reader has to sort of piece together everything that goes into these two approaches. They should instead be given more explanation in the Methods section.

3) The section on "Comparison between Different Prediction Methods" focuses on MD and MAD, but this somewhat masks the true scope of uncertainty. For instance, in Table 1, these metrics suggest the K_W/G comparison between ppLFER and SPARC is not much different than the K_WIOM/G comparison except for >5 functional groups. Claims by the author to the contrary are somewhat overstated. From the breakdown by functional groups and from Figure 1, though, it is clear there are some extreme or at least more varied cases. It seems relevant not only to ask "what is the average difference?," but also to ask "what is the probability that these two methods differ substantially?" Including as an additional figure a distribution (or cumulative distribution) of differences would help answer this question by showing not only average difference (the center of the distribution), but also the range of differences (the width and range of the distribution), and would strengthen the author's claims that there is a substantial difference in the uncertainty of these parameters.

4) In discussing atmospheric implications of different prediction methods, an important metric is the number (or fraction) of compounds that are in a different phase with dif-

ferent prediction methods, not just the number in each phase with each method as in Table 2. For instance, how many compounds that are condensed with ppLFER that "volatilize" with COSMOtherm? This would highlight the implications and importance of the differences.

Specific comments: p. 3 line 49: "number of organic species in the atmosphere is in the hundreds of thousands." Please cite your source, as these numbers often vary in the literature between thousands, tens of thousands, and hundreds of thousands, but probably only if including constitutional isomers with the same functional groups in different positions.

p. 3 line 58: Suggest including a reference to Compernolle et al., doi:10.5194/acp-11-9431-2011, which also explores this issue in some detail, specifically comparing various v.p. estimation methods used in this field

p. 4 line 76-78: Here and throughout the paragraph, it may be worth noting the expected uncertainties in some or all of these methods. The Hodzic approach suffers from fairly large scatter in the c*-H_eff trend. The authors also mention the cross comparison of GROMHE SPARC and HENRYWIN, and later cite a similar such comparison by Isaacman-VanWertz et al., but don’t mention the results of these comparisons here (several orders of magnitude discrepancy). This paragraph would better motivate the work by giving a quantitative discussion of previous estimates of variation across methods.

p. 5 line 97: Why not use all non-radical species in the MCM? Or is 3414 all of them? If not, what was excluded and why?

p. 5 line 107: Should be "units" instead of "unit

p. 6 line 122: Based on comments throughout the manuscript, it sounds like ppLFER includes some empirical calibrations- please elaborate a bit more on this approach.

p. 6 line 123: What is a "solute descriptor"? Please define

p. 6 lines 130-131: See general comment 2. A lot more information is provided about COSMOtherm than ppLFER or SPARC. Please provide a one-sentence description of what approach to these calculations SPARC takes

p. 7 lines 155, 162: It is a little confusing to including the Hodzic ranges in both their units and K_CP/G units. Consider sticking to the latter.

p. 7 line 158: To add clarity, consider reminding the reader of physical meaning when using statements like "higher K_WIOM/G", such as addeding a parenthetical "(lower volatility)".

p. 7 line 167: It would be worth pointing out early in this section that agreement between methods does not confirm or disconfirm accuracy. An easy first conclusion from Figure 1 is that COSMOtherm is just way off in K_W/G since the others agree. This is a conclusion the authors thoroughly discuss and debunk later, but it may help to guide readers away from this conclusion in the first place

p. 10 line 208: Again, consider adding Compernolle et al. to this citation.

p. 10 line 224: It overstates the data to claim that "K_WIOM/G is almost always smaller than one log unit". Of the 21 functional group comparison "bins" in table 1, 5 have MAD above 1 log unit, and another 4 have MAD between 0.9 and 1. So 20-40% of the bins fall outside or nearly outside this claim.

p. 13 line 282: "Partition" should be "partitioning"

p. 13 line 293-295: Here and below, the authors suggest that a lot of the issue with ppLFER lies in the limitations of solute description from ABSOLV, but do not discuss a means for improving this descriptors. What data would the authors need for this? This should be discussed, because if there is no way to get improved data, then this is an inherent limitation of ppLFER, or on the other hand it may be trivial to improve ppLFER in future work.

p. 14 line 326: Again, a little confusing to switch between K_CP, v.p. and C* in discussion

p. 15 line 330: Define or remove P_L

p. 15 line 351-352: Transition to the bulleted list is awkward. Change to: "However, we can infer that: - the fact.... - the generally...."

p.15 line 353-354: Again, it overstates the data to claim "KWIOM/G that are on average within one order of magnitude for all studied compounds" particular when including the claim "including highly oxygenated multifunctional organic compounds," which differ by 1.5-2 orders of magnitude between COSMOtherm and the others

p. 16 line 359: This is the first mention the ppLFER use real aerosols as a calibration reference. This highlights that information about what exactly goes into ppLFER is spread throughout the manuscript, it should be discussed in much more detail in the methods.

p. 19 line 439: See general comment 4. Quantifying the compounds that switch from condensed- to gas-phase between methods would provide more insight into the potential impact on SOA mass. Note that this is different than just the number of compounds in each phase with each method as in Table 2. A compound in the WIOM phase in all 3 methods doesn't "care" what method is used. Instead, the relevant metric for discussing SOA implications here and throughout the paragraph is changes in phase, in particular changes from condensed- to gas-phase.

Figures 1 and 2: Considering that much of the discussion is comparing difference in K_WIOM/G vs. K_W/G, it would be helpful to keep the top and bottom panels on the same y-axis scale. Also, in the headings of "Y vs X", generally X is on the x-axis and Y is on the y-axis, instead of the opposite used here

Figure 2: Gridlines on the major y-axis ticks would be helpful

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