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Interactive comment on "Novel methods for predicting gas-particle partitioning during the formation of secondary organic aerosol" *by* F. Wania et al.

Anonymous Referee #2

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[Attached PDF includes original formatting of the text]

General Comments

This manuscript deals with the description and evaluation of a group of alternative approaches to determining the equilibrium partitioning of organic compounds in the dry (non-aqueous) organic aerosol phase – authors refer to this as water insoluble organic matter (WIOM). Thorough comparison of the three techniques for a case study of OH-oxidation of n-alkanes is presented. The partitioning coefficients (Ki,WIOM per the authors' notation) are calculated for each of the oxidation products for the n-alkane

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reactions using the different techniques and are shown to compare quite well despite the differences in the underlying calculations. Of particular interest are their results demonstrating assuming a single surrogate compound for the WIOM phase and using a less computationally intensive approach seems to reproduce the results of a more fundamental calculation.

The work is certainly relevant and of great interest to the SOA community, as it proposes what amounts to a paradigm shift in the approach to determining the gas-particle particle partitioning of organic compounds in the ambient environment. The authors point out the lack of available data to assess vapor pressure predictions and do, to their credit, not ignore the same fact for their own proposed alternative approaches. If an experimental method were to be established for the direct measurement of Ki,WIOM, then the accuracy of their approaches could be assessed alongside vapor pressure estimation techniques and could feasibly be of great importance to the SOA community.

However, it will almost certainly be received critically as a result of the manuscript's overall tone. Additionally, the quantification of the extent to which the authors' methods are more precise than those typically used in the SOA community is questionable, and despite the authors' own caution against over-interpretation, these case-study results appear to be overgeneralized in a few places throughout the document.

Specific Comments

While the first 3 paragraphs recapitulate the authors' argument quite well, the remainder of the introduction is spent thoroughly repudiating the typical vapor pressure estimation techniques in the SOA community, which is not altogether surprising considering the aim of this manuscript. However, this sets the tone of the paper, which potentially undermines its reception amongst the target audience.

The subtle differences between the ppLFER, SPARC and COSMO-RS results (through 3.1.3) provide great insight into these alternative approaches, but it is noted earlier that they are "not really new" and that they have just "yet to be discovered and adopted by the wider SOA community" (pg. 21346, Ln. 24). Referring to these described methods as "novel" in the title, therefore, seems to suggest something that is not the case. The authors' own words also support this interpretation: pg. 21347, ln 2: ". . . we apply them here illustratively to the products of the OH-initiated oxidation of normal alkanes in the presence of NOx. . ." Why not use a re-wording of that as the paper title since it is more representative of the content? This change would also help soften the perceived tone of the manuscript.

Additionally, the predicted SOA yields by these methods are referred to as being both "as good or better" (in abstract and Pg. 21358, Ln. 13) and "for the most part better" than the vapor pressure estimation methods discussed (e.g. Jordan et al., 2008). Whereas this comparison was qualified elsewhere, it ought to be qualified in the conclusions section as well – particularly for readers that may skim more than others, so as not to mislead. Perhaps the conclusion and abstract should be re-worded, as this has not been demonstrated to be a general result.

The primary assertion of this manuscript is that Ki,WIOM can be predicted with "much greater precision" (Pg. 21364, Ln. 2) than vapor pressures for individual compounds. This does appear to be true based on the MAD (also known as mean average error, MAE in other contexts) values calculated between the different Ki,WIOM predictions here when compared against their selected literature values. However, it could be argued to be a tenuous conclusion for the following reasons.

[1]: The authors' logic appears to be: typical vapor pressure estimation methods have an expected MAD > 2 (Pg. 21346, Ln. 15), so as long as the alternative methods have MAD < 2, then they are more precise. The premise to that argument, though, is loosely defined as there are plenty of examples (in this paper's references no less) where different vapor pressure estimation techniques have MAD values on the order of those for the approaches advocated in this manuscript. If this "2 log unit" uncertainty comparison were to be made convincing, perhaps a different metric than the MAD should be used that better encapsulates the impact of outliers (like RMSE) despite

the fact that MAD/MAE are often used to assess the performance of vapor pressure prediction techniques elsewhere in the literature.

[2]: In another sense, the two quantities Ki,WIOM and vapor pressure do not have the same physical meaning, so should their variation be related in such a way? For instance, the activity coefficient and molecular weight variability between compounds is implicitly considered in the value of Ki,WIOM but not of vapor pressure alone. As another example, the manuscript cites Valorso et al., 2011 (pg. 21360, ln. 7) in its discussion. This study and the cited material consider different SOA systems and perhaps even different ranges of volatilities – something the authors should directly address in the manuscript. To that end, it would be interesting to see similar results for the alpha pinene system mentioned elsewhere in the paper.

[3]: Regarding the range of aerosol volatility: how is the ‘atmospherically relevant’ range of Ki,WIOM determined? Using the manuscript’s supplemental information and converting the units of KâĂši,p to m3 μg-1 (i.e. Kp of Pankow 1994, Atmos. Environ., 28, 185-188), the following equation for an equivalent (approximately) saturation mass concentration (in μg m-3) can be obtained: Cˆ*=1/K_p =_aerosol/(K_WIOM ãĂŰ10ãĂŮˆ(-6))=ãĂŰ10ãĂŮˆ12/K_WIOM

Where the density of aerosol is in units of g m-3 (using a value of 106 as in the manuscript, pg. 21353, ln. 15) would suggest that for log(Ki,WIOM) = {$\sim$9.5, 15} (e.g. Figure 5), the equivalent C* = {$\sim$300, 10-3}. This is consistent with the typical range of ambient organic aerosol and in the range of what are referred to by some as SVOCs and LVOCs (Pandis et al., Faraday Discuss., 2013,165,9-24). The authors may wish to clarify this otherwise in the text if this explanation is not satisfactory.

Note: these C* values equate to, when roughly converted (assuming ideal gas and Mw = 0.2 kg mol-1), log(P, atm) of about -5 and -10. This range is not the same as presented in Valorso et al. (-13 to -5), and perhaps more interestingly the domain of their investigated log(P, atm) was -30 to 0 while the equivalent range for this study

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would be (if calculated as above) −11 to 3, potentially calling into question the values cited on pg. 21360, ln. 12 as incomparable. Of course, the authors could point out that a proportional relationship between vapor pressure and Ki,WIOM does not necessarily exist given potential variation in the activity coefficient for different compounds in the WIOM phase. Although, such an argument would lend credence to the previous point [2].

A final note regarding the manuscript is its generalizability, as this manuscript presents only one case study. The proposed alternative approaches are indeed presented in an appealing fashion, and although the authors may be leaving this to a follow up manuscript, they mention additional calculations carried out on the alpha pinene SOA system using Chen & Griffin (2005) oxidation products as a starting point that are not shown – for good reason of course (pg. 21362). It would support the methods' generalizability to see a similar analysis as the case study presented here done for the alpha pinene system using the products from Valorso et al. (2011) or a contemporary. It may also help justify the choice of the MAD values the authors' use for comparison in section 4.1.

Technical Comments

In general, there is an odd word choice throughout the document (e.g. "eschew") that would not aid non-native English speakers in interpreting the contents of the manuscript. The authors may wish to adjust the text to account for this.

Pg. 21342, Ln. 17: "…vapor pressure estimates, the predictions between the Ki,WIOM estimates do not deteriorate…" Subject/verb agreement & sentence fragment.

Last sentence of abstract: Remove the phrase "or the assignment of SOA-forming molecules to volatility basis sets." This point is not mentioned in the manuscript. If the authors would rather elaborate on this topic, it should be separate from the discussion of predicting vapor pressures, as that is not the goal of the VBS approach.

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Pg. 21344, Ln. 8: “In particular…” – sentence is difficult to follow due to wording. Consider rewording for readability.

Pg. 21344, Ln. 22: Could the authors clarify what it means to be “more accurately accessible?” This is related to the discussion of accuracy vs precision above.

Pg. 21348, Ln. 3: Typo? Change “Eq. (1)” to “Eq. (3)”

Pg. 21348, Ln. 16: Very long direct quote regarding SPARC. Suggest summarizing.

Pg. 21348, Ln. 27: For readers unfamiliar with SMILES, perhaps it would be better to introduce this material, or at least define the acronym and provide a citation for background.

Pg.21353, Ln. 18: Modify equation numbers from “(2) and (3)” to “(4) and (5)” as the reference here is incorrect.

Pg. 21355, Ln. 10: “Table S2” should be “Table S1” – I assume, as there is only one table in the supplement.

Pg. 21356, Ln. 10-12: Remove sentence beginning “Considering the uncertainty…” or provide some supporting quantification of the inherent uncertainty.

Pg. 21356, Ln. 12-19: Whereas KOAWIN in EPISuite relies on a relationship between the air-water-octanol partitioning of a substance, this study does not take into account the possible existence of an aqueous phase. Could the way that the octanol-air partitioning coefficients are calculated therefore be inherently different so as to preclude a direct comparison?

Pg. 21356, Ln. 15: Figure S1 in supplement only shows comparison between SPARC and EPISuite, not ppLFER.

The last two paragraphs of section 4.1 are somewhat redundant and could be condensed / combined with the approach descriptions in the methods section.

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Pg. 21361, Ln. 23: Comma splice at . . . “here is promising, but should”

Pg. 21363, Ln. 1: Reword the sentence for clarity & grammar . . . “make to the formation of SOA”

Pg. 21363, Ln.12: What does the phrase “conceptually simpler and therefore more elegant” add to the value of the discussion of these alternative approaches?

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C7429/2014/acpd-14-C7429-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 21341, 2014.