Atmos. Chem. Phys. Discuss., 14, C9452–C9455, 2014
www.atmos-chem-phys-discuss.net/14/C9452/2014/

Atmospheric Chemistry and Physics Discussions
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Interactive comment on "Using the chemical equilibrium partitioning space to explore factors influencing the phase distribution of compounds involved in secondary organic aerosol formation" *by* F. Wania et al.

Anonymous Referee #1

Received and published: 24 November 2014

The manuscript by Wania et al. presents a graphical approach to evaluating phase partitioning of organic compounds in complex (multi-phase) systems relevant to formation of secondary organic aerosol (SOA). The potential benefits of such an approach, described by Wania et al., are the ability to simultaneously consider multiple factors influencing phase partitioning and their relative importance. The factors that can be considered include atmospheric variables (e.g., temperature and liquid water content) and chemical properties of the condensing compounds and absorbing phase (e.g., molecular size and functionalization). One of the most attractive features of this graphical approach, as it is presented, is its use for prioritizing data gaps. The authors suggest that the graphical approach can be used to identify parameters/conditions for which some uncertainty can be tolerated and others for which better constraints are needed. Another attractive feature is the use of models that predict partitioning explicitly, eliminating the need for separate (and highly uncertain) estimations of saturation vapor pressures and activity coefficients. This appears to be the subject of a companion manuscript also under review in ACPD. One potential limitation of this approach is the ability of one modeled system to represent partitioning behavior under diverse ambient conditions (discussed further below).

There is much interest in improving model representations of SOA formation, including simultaneous consideration of multiple phases. Efforts are greatly needed to reduce uncertainty in existing approaches. The manuscript is thus highly relevant within the scope of ACP. However, it is not clear that the graphic approach presented truly represents a significant contribution to the field, and that it is substantially different from existing approaches and analyses. It is recommended that the manuscript be reconsidered for publication in ACP following attention to the comments on scientific and presentation quality provided below.

Technical Comments Scientific quality: One of the biggest concerns with the graphical approach as written, is the consideration of partitioning between an aqueous (mostly water?) and a water insoluble organic phase. It is known that organic particulate matter can be up to 80% water -soluble (e.g., Sullivan et al., GRL, 2004). It is not clear exactly how this substantial component of the absorbing phase is conceptualized within the presented approach. Is the aqueous phase an aqueous+organic phase (as seems to be supported by the discussion of the disappearance of the WIOM phase in section 2.4)? If this is the case, at what point is that phase considered an organic phase and how are the properties along this continuum (mostly aqueous to mostly organic) to be treated in the presented approach? Or is the water insoluble phase a water insoluble and/or water-soluble phase? This latter description seems more likely given the choices of surrogate structures for “WIOM” in SPARC, as well as use of organic aerosol load (Eq 8) to determine the size of the “insoluble” absorbing phase. If this is the case, why isn’t the organic phase referred to more generally as an organic phase (that spans a continuum between insoluble and soluble organics represented by some end members)? It is not clear from the manuscript, as written, that the likely compositions of phase(s) are well understood and well represented by the current application.

p. 26556, line 10-15: How do the measured KWIOM/G values vary by sampling location (urban to coastal)? Why are these values averaged? It seems valuable information on composition dependent partitioning is being lost. Do the model comparisons improve/worsen if individual values are used instead of an average?

p. 26556, line 21: If the goal is to better understand atmospheric SOA formation, why are different solvents considered for different partitioning compounds? Are distinct regimes expected under atmospheric conditions? If so, this needs further explanation/clarification in the manuscript.

p. 26562, section 3.3: There seems to be two types of uncertainty represented between the three models that are not clearly differentiated in this discussion. One is the unknown properties of the solvent, as represented empirically (in ppLFEr) or by surrogate(s) (in SPARC/COSMOtherm). The other is uncertainties associated with calculating phase partitioning using a semi-empirical approach (SPARC) vs. a quantum chemical approach (COSMOtherm).

p. 26548, line 22: How do lower temperatures shift the partitioning of more volatile organics to the gas phase?

Discussion: Given the relatively large number of “visualization” spaces that have been proposed and presented for representing SOA, could a similar analysis be presented in the context of existing representations (rather than introducing a new one)?

Editorial Comments Presentation quality: The introduction is somewhat poorly written and could be revised to build confidence in the approach presented by the authors. Clarity in the first paragraph could be improved by first discussing environmental/atmospheric variables together and then chemical properties and their interactions (for example as grouped in the abstract). Also, it is suggested that consistent terminology be used to describe the phases and partitioning compounds (condensed vs. aqueous vs. particle). For example, it is not clear why, on page 26548 line 20, the authors are discussing gas/aqueous phase equilibrium. Typically higher molecular weight organics would be expected to partition to a mostly organic phase.

26548 line 8: Size and polarity influence the extent to which compounds prefer the gas or particle phase, but it isn't an either/or for the semi-volatile compounds as written. It also isn't clear (as written) that the gas and condensed phase(s) together make up the aerosol, and the compounds of interest are continuously shifting (to some degree) between these phases.

It is suggested that the assumptions of the chemical partitioning space (2.4) be presented before the discussion of partitioning coefficients (2.3).

p 26558, line 10: replace "acknowledged" with "accepted"

p 26565, line 17: The statement that SPARC predictions for highly polar solvents should be considered suspect seems like an over generalization and not necessarily well supported by the results.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 26545, 2014.