Atmos. Chem. Phys. Discuss., 8, S689–S692, 2008
www.atmos-chem-phys-discuss.net/8/S689/2008/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Organic particulate matter formation at varying relative humidity using surrogate secondary and primary organic compounds with activity corrections in the condensed phase obtained using a method based on the Wilson equation" *by* E. I. Chang and J. F. Pankow

Anonymous Referee #1

Received and published: 12 March 2008

This paper describes a new model to calculate partitioning coefficients needed to simulate gas-particle partitioning of organic aerosols. The model is an extension of the current two component, lumped parameter absorptive partitioning model developed by Pankow and widely used in air quality models. This paper extends this approach by proposing an efficient scheme to evaluate activity and mean molecular weight. It does this by assigning surrogate species to each of the lumped parameters and then using a modified Wilson method to calculate the activity coefficients. Conceptually what the authors are doing is reasonable straightforward, but I had a very hard time following the details in the paper of how it was done. I like the group contribution based approach. This seems essential given the complexity of organic aerosols; it also nicely builds on the recent SIMPOL model of Pankow. Overall I think that this paper makes a valuable contribution to the surrogate based approach to calculate gas-particle partitioning.

Below are some suggestions for how the paper could be improved; after addressing these, the paper is suitable for publication in ACP.

I found it very hard to follow the details of the derivation. I would encourage the authors to rewrite sections of the paper (2.1, 2.3, 2.4) and try to make things clearer. For example, it was not clear to me exactly what was done in section 2.1. Maybe a paragraph at the start clearly stating what are the inputs of the calculation and what are the outputs? Then go into the mdeoth. You seem to be deriving the values in Table 1 using assumed structures and chamber measured Kp. You are using SIMPOL to determine Po? What is the parameter omega? You seem to be iterating on that, but I could not figure out where it was defined.

Along these lines, the footnotes for Table 1 seem messed up. For example, was P(L,o) for SOA derived from equation 13?? Presumably Ci was derived with equation (13), but the footnote says it was related to KP,i?? etc.

Model evaluation – I am always concerned when there is extensive model development with little or no model evaluation. I realize that the data truly need to evaluate the model do not exist; however there is a large body of chamber SOA data and some POA partitioning data. How well does the new model do in reproducing those data? Although I understand there are lots of concerns about atmospheric relevance of chamber data, that at least is a place to start. Comparisons are presented with a little chamber data, for which both the new and the standard model perform similarly. (Al-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

though I understand that these data may not be the strongest test because the deltaHC was so large).

Another seemingly important application of the model that is not exploited here is to help identify specific experiments that would be useful to test the standard model. It seems like a key question is are activity and MW effects really important in atmospheric aerosols? If so, then we need the more sophisticated model and the associated large effort required to measure all of the data needed to implement it. For example, the paper makes a big deal that increasing relative humidity could bias partitioning estimates of the standard model because of activity and mean molecular weight effects. However, the Cocker et al. data presented here do not support this conclusion. It seems like someone should go out and do that – this would be more likely if this paper more clearly stated that. What other experiments could be done to test whether or not the issues addressed by the new model are important.

One potential issue on using a small number of surrogate species models to simulate complex mixtures is entropic effects. Organic aerosols are thought to be made up of thousands of individual compounds all present at low concentrations. What are the implications for that in terms of phase separations and activity effects? You have fit this model using binary mixture data (page 13), what is the likelihood that binary mixtures of these surrogates represent the actual behavior of a very complex mixture. As the mixture complexity increases Marcolli et al. (Journal of Physical Chemistry A 2004, 108(12), 2216-2224) suggest that phase separations may not be as likely. Could you be overstating the important of these effects due to the simple mixtures the model is considering?

Abstract - The last sentence seems premature. It seems like the first need is actually test the model predictions against the available SOA and POA partitioning data. If the model does a reasonable job at reproducing that data then it makes sense to implement it.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Page 11. Is it a problem that the set of groups used by the CP-Wilson method and the SIMPOL model are not the same? Wouldn’t it be better if they were?

Page 15. I was confused how the model determines that two phases exist. I understand the gibbs free energy basis for determining phase separation, but it was not clear to me how this was implemented.

Page 15. The statement that partitioning data are not available for POA is not correct. Shrivastava et al. (Environmental Science & Technology 2006, 40(8), 2671-2677) published fits for diesel and wood smoke data with a 2 component lumped parameter absorptive partitioning model. Robinson et al. (Science 2007, 315, 1259-1262) fit diesel data with a basis set. These data are similar to SOA chamber data. At a minimum the authors should acknowledge this in the paper and make some qualitative comparisons of the values that have assumed relative to what has reported in the literature.

Page 20 paragraph starting with "Table 6 provides" You seem to be claiming that the similarity results between CP-Wilson and UNIFAC supports the view that errors in prediction of various gross parameters are not large. However, this does not seem like an independent test since you have fit the CP-Wilson 1 with UNIFAC. Doesn’t this just say that the CP-Wilson.1 gives is a reasonable parameterization of UNIFAC?

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 995, 2008.