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Comment

Interactive comment on “Temperature-induced volatility of molecular markers in ambient airborne particulate matter” by C. R. Ruehl et al.

Anonymous Referee #2

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This manuscript presents the results of volatility of selected organic molecular marker compounds sampled at ambient and heated ($\sim 10\text{K}$) temperatures at an urban and a rural location in the summer and winter. The paper is introduced by a discussion of the volatility of molecular markers, noting that they should evaporate at approximately the same rate as the total particulate matter to meet the conservation requirement for source apportionment models. The main focus of the paper, however, is to use the volatility of the molecular markers as a probe for estimating the activity of the bulk particulate matter relative to the marker compound, and to determine the deviation of the bulk particulate matter from ideal solution, which is the model of partitioning theory. The paper should be published after major revisions described below, which mainly focus on a) giving a clearer picture of the model of aerosol and volatility regarding sources, absorption, gas-phase oxidation, and mixing state, b) clarifying the message

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of the results by refocusing the introduction and adding conclusions, and c) correcting inconsistencies in some parts of the paper.

Main Points

1) The concept being explained in this work regarding the reasons for volatilization (or not) of the organic molecular markers from the particle phase seems to involve at least the following processes: emission from sources, absorption/adsorption/evaporation between particles and the gas phase, secondary processing in the gas phase, and mixing state of the absorptive/adsorptive aerosol surfaces. However, the authors do not clearly state their model for the relationship between these processes and how they impact the framework for the measurements from this study. Some of this framework can be discerned from the text, but not all of it. For the main example in the paper, *n*-alkanes are a marker for vegetative detritus. What is the expected difference in the strength of this source between summer and winter (pg. 20340 Line 13, "... the emissions sources of these compounds do not undergo five-fold increases in the summer vs. winter..."), or between the urban and rural sites? What do the authors think then happens to the *n*-alkanes? They could stay in the primary particles (is this near an ideal solution for these compounds?) or evaporate. Vapor-phase molecules could be oxidized (and thus removed from the system of consideration) or perhaps recondense onto other particles. Now the character of the surface of the particles comes into play. Does the mixing state of primary and more oxidized particles affect the potential uptake, or can internal mixtures be assumed? A clear model for these processes would clarify the authors' model to the reader and provide a better context for considering the concentration and volatility differences between the seasons and sites.

2) The motivation of the paper as described in the introduction is driven by the appropriateness of molecular markers for source apportionment, asking the question, "Do molecular markers evaporate at same rate as primary PM?" But the results of the present study do not give an answer to this question. Rather, the manuscript uses volatility of selected molecular markers as a way to estimate the activity of the solution

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into which the markers can absorb. The addition of a conclusions section would give a good opportunity to summarize both of these points for the reader.

3) Last sentence at end of Sect. 2 (pg. 20334 Lines 26-27) seems to set the context for the focus of this paper. I suggest that this be moved or added to the introduction and that it be tied in better in the discussion section, with the discussion of Fig. 6, and in the suggested conclusion section.

4) There are several inconsistencies between parts of the text. Example 1: The experimental description of sampling (summer urban 2006, winter urban 2007, summer rural 2007, winter rural 2008) doesn't match the data shown in Fig. 3ab (summer urban 2006, 2008, 2009; winter urban 2007, 2009, 2010; summer rural -none-; winter rural 2008). Example 2: Fig. 1 has curves for a C5 diacid absorptive surface, but the text in the discussion refers to this as succinic acid (Pg. 20342 lines 14, 27), which is a C4 diacid. Example 3: Hopanes are not shown in Fig. 4 (Pg 20342 Line 26).

Detailed Points

1) Pg. 20330 Line 13: I suggest adding a line here to remind the reader that volatility depends on both the molecule that may evaporate and the characteristics of the absorptive surface to provide an introduction to the next two sentences.

2) Pg. 20335 Lines 3-20: This paragraph does not actually describe the experimental conditions of this experiment and should be moved to introduction.

3) Pg. 20335 Line 25-26: A clarification about the sampling procedure may be helpful here. Were the filters left in the samplers continuously for the 5 sampling days, but the samplers were only run (i.e., pumping) during the sampling hours? If so, how might temperature and relative humidity of the samples overnight affect the volatility of compounds of interest? Were the samplers in a climate-controlled environment?

4) Pg. 20335 Line 27 and Pg. 20336 Line 4: The former instance says that two sample pairs were collected, but the latter instance says that three samplers were operated

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simultaneously. Why were only two samples used from three samplers?

5) Pg. 20337 Line 5: It may be useful to clarify that "heating" here means heating of buildings, as opposed to sample heating.

6) Pg. 20339 Lines 2, 26: Is Westside the rural site? It is not named in the Experimental section.

7) Pg. 20340 Line 16: Steranes do not have the same volatility trend as n-alkanes and hopanes according to Fig. 5.

8) Pg. 20340 Line 21-23: It seems that C_{POM} should be known to the authors as this statement need not be phrased as conjecture.

9) Pg. 20341 Line 19: It seems that other surrogate organic phases would give results similar to 5-oxo-pentanoic acid, not similar to OOA.

10) Fig. 1: This figure would be clearer if it was composed in two panels with C^* in one panel and f_{lost} in another. The meaning of the colors and dashes of the lines are not explained well in the caption or the figure. Colors appear to go with the type of absorbing phase, so should "ideal, +8K, 50% abs" line be black? If dashes go with the degree of heating (as is the case for the ideal solutions), then all lines for +8K should be solid. It would be interesting to add one or two of the model HOA/OOA mixtures from Fig. 6 to this figure, since the curves in Fig. 6 are not directly comparable to those in Fig. 1.

11) Figs. 2 and 5: What are the percentiles of the whiskers?

12) Fig. 3: In panels (a) and (b), it is very difficult to see the symbols for most of the points. For example, it is very difficult to see how EC and OC vary by season. Perhaps the confidence bars could be thinner, and/or the points colored by season? In (c)-(e), what is the meaning of the underlined numbers?

Typos and Grammar

1) Pg. 20334 Line 15: Suggest changing "to satisfactory model" to "for satisfactory modeling of" or "to satisfactorily model".

2) Pg. 20335 Line 26: change "heath" to "health".

3) Pg. 20342 Line 27: change "at" to "as".

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