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Atmospheric Chemistry and Physics Discussions

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

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This manuscript presents the results of volatility of selected organic molecular marker compounds sampled at ambient and heated (_10K) 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 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 no 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 cites.

R: We agree that emissions do not vary by a factor of five. We attribute the higher concentrations in the summer to the presence of a more prevalent, relatively non-polar phase which is available to absorb the alkanes. We have added a conclusions section

to the paper, as suggested, which we hope explains this logic more clearly.

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 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.

R: As stated before, we have added a conclusions section. It is true that we cannot directly answer the question mentioned by the reviewer, because we have only complex ambient samples and no source-specific samples that would be required to do so. We now end the paper with a recommendation that such studies be conducted in the future to help answer the question. Also, we feel that our results do suggest that the answer to the question may be "no" (as stated in the conclusion).

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.

R: We have moved this sentence to the introduction.

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).

R: We have added the following text to the experimental section to clarify this: "In addition to the field campaigns mentioned above, we also include limited data from

subsequent campaigns at the Fresno site, including the summer of 2008 and 2009, and the winter of 2009 and 2010. These data consist only of bulk carbonaceous fractions - specifically, elemental carbon and organic carbon (see section 3.2), and do not include any compound-specific analyses." Also, we have added this following text to the caption for Figure 3: "Note that for [EC] and [OC], data from additional field campaigns has been added to reduce the error in the linear regression, and also that [EC] and [OC] were not determined in the heated leg of the rural summer samples due to lack of material."

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.

R: We have corrected this, it now reads "glutaric acid"

Example 3: Hopanes are not shown in Fig. 4 (Pg 20342 Line 26).

R: We have corrected this.

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.

R: We have added such a line.

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

R: This change has been made as requested.

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?

R: We have added the following clarifying line: “At other times, filters remained in the samplers, but we turned off all pumps and heaters.” This was done because of the potential for contamination involved with multiple removing and reloading of the filters. The samplers were not climate controlled, but were located in the shade, and thus the temperature inside the sampling cabinets remained below ambient. Because of this, and the fact that the samplers were operated during the daytime, it is unlikely that the filters experience higher temperatures in the evening/overnight than they did during active sampling.

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

R: We have added the following italicized text for clarification: “Two sample pairs were collected (for a total of ten days) in each season at both locations for a total of 16 samples. . .. Three separate RAAS samplers were operated simultaneously, each with an “ambient” leg and a “heated” leg wrapped in electrical resistance heating tape. For compound-specific analyses, filters from these three samplers were composited; however, for bulk analyses (i.e., elemental and organic carbon), measurements were made of each individual filter.

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

R: We have added the phrase “either residential or commercial” for clarification.

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

R: We now consistently refer to “the urban site” and “the rural site” to avoid confusion.

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

R: We have removed “steranes” from this line, since they were not detected at the rural site.

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

R: We have changed CPOM to Cabs (concentration of the absorbent) in this and other points in the text. While it is true that we have measured CPOM, which should be an upper bound for Cabs, it is possible that the total POM is divided into two phases, only one of which is capable of absorbing large alkanes.

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.

R: We agree and have made this change.

10) Fig. 1: This figure would be clearer if it was composed in two panels with C* in one panel and flost 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.

R: We have split Figure 1 into two panels as recommended, and modified the caption. We considered a version of this figure that included HOA/OOA mixtures but decided that it was too complicated. Also, using the group contribution activity coefficient model, one can shift the flost vs. carbon number curve to the left or the right either by varying diacid size or the relative proportions of HOA and OOA surrogates, so essentially no new insight is gained by including both. Finally, we have adjusted the color and line style to be more consistent, as suggested.

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

R: 10/90%. This has been added to the captions.

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?

R: Underlined values indicate rural samples (this has been added to the caption). Also, we have made the error bars thinner and the symbols larger in panels (a) and (b).

Typos and Grammar 1) Pg. 20334 Line 15: Suggest changing ”to satisfactory model” to ”for satisfactory modeling of” or ”to satisfactorily model”.

R: We have rewritten this line.

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

R: Done. 3) Pg. 20342 Line 27: change ”at” to ”as”. R: This paragraph has been removed.

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