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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 paper describes an experimental study of the volatility of select organic molecular markers. The study collected a number of ambient filter samples at an urban and a rural site during the summer and winter. During each sampling period they collected parallel sets of filter samples: one at ambient temperature and a second at nominally 10K above ambient T. They estimated the volatility of markers by comparing concentrations of n-alkanes, hopanes/steranes, levoglucosan, and PAHs on the two sets of samples. The paper shows significant loss of hopanes/steranes and many n-alkanes with mild heating, demonstrating that these compounds are semivolatile in the atmosphere. This finding has important implications for the atmospheric lifetime of these compounds and their use in receptor models. In contrast, the paper reports relatively

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little effect of gentle heating on PAH concentrations. Therefore they conclude that different mechanisms (adsorption versus absorption) control the gas-particle partitioning of PAHs and alkanes. The data are very interesting and should be published. However, in places I feel that the paper over-interprets/speculates about some of the results. Here are some specific areas that need improvement.

Major comments The paper in numerous places makes claims about compounds being less volatile and more volatile. However, without gas phase measurements it seems very difficult to draw this conclusion. An example of this problem is on page 20342 line 29– “less volatile in winter” How do we know they are less volatile in winter? For example, flost could be smaller in the winter because a larger fraction of the compounds exist as vapors in the winter (meaning the compounds are more). This scenario is illustrated by the flost curve in Figure 1 for the C-5 diacid case; the C^* of the alkanes is much higher than the ideal case for this sorbent. Note this change in partitioning might also explain the summer-winter variation in alkane concentrations.

R: We agree, and in fact this is our interpretation of the results (that a greater portion of the semi-volatile compounds are in the gas phase during winter). We have been using the word “volatility” to mean “greater tendency to evaporate” (i.e., higher flost), but now appreciate that this is confusing because many would assume that “more volatile” means “greater percentage in the gas phase.” We will change the language in the paper – for example, “less volatile in winter” will be changed to “lower tendency to evaporate during winter.”

The paper reports significant seasonal and urban/rural differences in partitioning. The paper tries to explain these differences (pages 20341-20342) but this discussion was highly speculative. At least three potential issues were raised polar/non-polar absorptive partitioning, adsorptive partitioning, and the potential role of water. However, there essentially no evidence presented to support this discussion. This section of the manuscript should be shortened. For example, the previous paragraph provides another plausible explanation for some of the trends in partitioning.

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R: We feel that our group-contribution activity coefficient modeling, which we relate to recent results from high-resolution aerosol mass spectrometry, supports the claim that the polarity of the absorbent can explain rural-urban differences in volatility. However we agree that the discussion of adsorption and water content lacks supporting evidence, and we have removed it.

The calculations shown in Figure 1 have some important implications for both experimental design and interpretation of the data. For example, the figure shows a high flost for compounds that likely exist as vapors in the atmosphere (e.g. C₂₀ n-alkanes). Given all of the issues with artifacts and filter sampling it is not clear that the authors can accurately measure flost (in particle compounds) for compounds that exist 95%+ in the vapor phase. This seems to be a significant weakness in the experimental design and it needs to be pointed out of the manuscript.

R: It is true that reported values of flost are likely not very meaningful for compounds such as a C₂₀ n-alkane which exist overwhelmingly in the gas phase. We have added the following text making this point: “It is important to understand that the change in flost with carbon number is most meaningful in the region of the curve where flost changes sharply with carbon number. It is at this point where C* is closest to C_{abs}, and thus where significant material exists in both the particulate and gas phases. At lower carbon numbers (i.e., approximately C₂₀), almost all material exists in the gas phase, and therefore the ability to constrain flost is limited”

Minor comments Figure 1. This is a nice figure, but it seems un-necessarily complicated. It has two y-axis and multiple curves. It took me a while to figure out which curve went with which y-axis. The figure would be much easier to interpret if it was broken into two panel, e.g. a top panel with the C* curves and a bottom panel with the flost curves.

R: We have taken this suggestion and split Figure 1 into two panels accordingly.

Figure 4. Why are the concentrations of large alkanes so high on the ambient back-

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up filters? E.g. a C32 and larger exist pretty much exclusively in particle phase but concentrations on the front and back up filters are comparable? This suggests that there may be a blank problem in the dataset.

R: We did not see these larger n-alkanes in field blank filters, only on the backup filters. Our group-contribution activity coefficient modeling suggests that if the organic aerosol is relatively polar, even larger n-alkanes will exist either in the gas phase or perhaps adsorbed onto particles. Thus, while it may seem counter-intuitive that such a large molecule could exist in the gas phase, we think it is plausible that the presence of these molecules on the back-up filter could result from gas-phase adsorption.

Page 20304 line 12- factor of five increase in summer hopanes concentrations. It is hard to see partitioning (alone) causing such a large change in concentration. Assuming that atmospheric concentrations are, on average, nominally the same in both seasons (i.e. constant emissions) then it implies that at least 80% of the hopanes exist in vapor phase in winter but none exist as vapors in the summer. This would require a very large change in amount of sorbing phase. Note that results from the Eastern US show the opposite seasonal pattern in hopanes (e.g. Zheng et al. EST 2002; Subramanian et al. AE 2006)

R: We agree, but also note that the seasonal difference is likely due to a change in both the amount and composition (i.e., polarity) of the absorbent. Also, we note that limited rain was experienced during both winter campaigns, and that this could also have contributed to the lower concentrations in the winter.

Page 20337 line 15 Difference in summer and winter n-alkane concentrations. Biogenic emissions may contribute significantly to summertime n-alkane contributions. Is there evidence of this in, e.g., CPI analysis?

R: CPIs were 1.6 during the urban summer and 2.9 during the rural summer campaigns, suggesting a minor but significant contribution from leaf waxes. We believe the use of the 1.8 μ m cyclone removed the majority of leaf detritus particles.

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Clarifications 1. Was the temperature monitored downstream of the backup filter.

R: Yes, the quoted temperature increases (9.6 ± 2.1 and 8.2 ± 2.7 K) were measured by thermistors immediately downstream of the backup filter.

2. What was the residence in the heat zone upstream of the filter? Are there concerns that the sample had not reached equilibrium?

R: The residence time in the heated tube upstream of the collection filter is a few seconds, but the collected particles are then exposed to heated air for an average of 2.5 hours during the 5 hour collection period. Equilibrium should easily be achieved during this time.

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