

Interactive
Comment

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

Anonymous Referee #1

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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 little effect of gentle heating on PAH concentrations. Therefore they conclude that different mecha-

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nisms (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.

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.

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

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the vapor phase. This seems to be a significant weakness in the experimental design and it needs to be pointed out of the manuscript.

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.

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

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)

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?

Clarifications 1. Was the temperature monitored 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?

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