**Atmospheric
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Temperature-induced volatility of molecular markers in ambient airborne particulate matter

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Abstract

Molecular markers are organic compounds used to represent known sources of particulate matter (PM) in statistical source apportionment studies. The utility of molecular markers depends on, among other things, their ability to represent PM volatility under realistic atmospheric conditions. We measured the particle-phase concentrations and temperature-induced volatility of commonly-used molecular markers in California's heavily polluted San Joaqin Valley. Concentrations of elemental carbon, organic carbon, levoglucosan, and polycyclic aromatic hydrocarbons were not reduced by mild (~10 K) heating. In contrast, both hopane/sterane and n-alkane concentrations were reduced, especially during the summer sampling events at the urban site. These results suggest that hopanes and steranes have effective saturation concentrations ~1 µg m^{-3}, and therefore can be considered semi-volatile in realistic ambient conditions. The volatility behavior of n-alkanes during the urban summer is consistent with that predicted for absorption by suberic acid (a C_8 diacid) using a group contribution modelling method. Observations can also be matched by an absorbent whose composition is based on recently-obtained high-resolution aerosol mass spectrometer factors (approximately 33% "hydrocarbon-like" and 67% oxygenated organic aerosol). The diminished volatility of the n-alkanes, hopanes, and steranes during rural and/or winter experiments could be explained by a more oxygenated absorbing phase along with a non-absorptive partitioning mechanism, such as adsorption to soot. This suggests that the temperature-induced volatility of large hydrocarbons in PM is most important if a relatively non-polar absorbing organic phase exists. While the activity coefficients of most organic aerosol compounds may be close to unity, the assumption of ideality for large hydrocarbons (e.g., hopanes) may result in large errors in partitioning calculations.

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1 Introduction

The design and evaluation of strategies to mitigate the negative effects of airborne particulate matter (PM) require source apportionment information. Statistical source apportionment techniques rely on the chemical signatures measured at receptor sites
5 to quantify primary source contributions. Organic molecular markers have been especially useful for the source apportionment of carbonaceous aerosols (Schauer et al., 1996; Chow and Watson, 2002; Lin et al., 2010). Commonly-used organic molecular markers include hopanes and steranes for motor oil emissions (Simoneit, 1999; Phuleria et al. 2007; Riddle et al., 2008); heavy polycyclic aromatic hydrocarbons (PAHs)
10 for gasoline exhaust (Riddle et al., 2008) and coal combustion (Robinson et al., 2006); light PAHs for diesel exhaust (Fraser et al., 2003; Riddle et al., 2008); cholesterol for food cooking (Rogge et al., 1991); n-alkanes for vegetative detritus (Rogge et al., 1993); and levoglucosan for biomass burning (Simoneit, 2002). In general, the utility of a marker compound depends on how unique it is to a source, and how conserved it is
15 in the atmosphere (i.e., its volatility and/or reactivity) relative to the other primary mass emitted from that source.

Recent smog chamber experiments have suggested that molecular markers and some portion of primary PM emissions may be semi-volatile (Robinson et al., 2007; Lambe et al., 2009). These experiments have indicated that evaporation of primary
20 emissions is coupled to their gas-phase oxidation (Lambe et al., 2009; Miracolo et al., 2010), in part because photochemical lifetimes of larger, non-polar molecules in the gas phase (Atkinson and Arey, 2003) tend to be shorter than the timescale of diffusion of oxidants (e.g., the hydroxyl radical) to particles. This suggests that the volatility of primary molecular markers may also largely determine their stability in the atmo-
25 sphere. Ideally, molecular markers from each source would evaporate (and/or react) at the same rate as the primary PM from that same source. Any mismatch between the volatility of the molecular markers and the primary PM mass could cause an under-prediction or over-prediction of source contributions. In some ways, the importance of

molecular marker volatility has already been recognized. Several molecular markers formerly used in source apportionment calculations have been omitted from more recent studies due to their volatility (e.g., retene, Ramdahl, 1983 vs. Schauer and Cass, 2000). Still other studies have suggested that light semi-volatile PAHs may be too
5   strongly bound to the particulate phase for significant volatilization to occur (Arp et al., 2008; Pankow and Bidleman, 1992). These examples illustrate the difficulty in using simple theories and/or smog chamber measurements to make a priori predictions about the most appropriate molecular markers for source apportionment studies in the real atmosphere. A need exists to quantify the volatility of molecular markers under
10 realistic atmospheric conditions.

In the present study, urban (Fresno) and rural airborne PM samples from the San Joaquin Valley (California) were collected to study the volatility of commonly-used molecular markers. Collection occurred at ambient temperatures and at approximately 10 K above ambient, during both the summer and winter. Samples were analyzed for
15 thermo-optical elemental and organic carbon (EC and OC) concentrations. Molecular markers including PAHs, hopanes, steranes, levoglucosan, cholesterol, and n-alkanes were quantified by solvent extraction followed by gas chromatography-mass spectrometry (GC-MS). We compare the results between the ambient and heated samples, to determine if and when volatilization reduces particle-phase concentrations of molecu-
20 lar markers. We also use a group-contribution activity model (Gmehling et al., 1993) to compare different assumptions regarding the composition of the absorbent to observations, using observations of n-alkane volatility. Many researchers have assumed that absorption forms an ideal solution; we test this assumption in ambient aerosols by calculating the activity of n-alkanes in various model absorbents.

25 ## 2   Absorptive partitioning theory

According to standard absorptive partitioning theory (Pankow, 1994), the concentration of a semi-volatile compound i in particulate organic matter (POM) depends on its total

(gas+particle) concentration ($C_{i,\text{tot}}$), its effective saturation concentration (C_i^*), and the concentration of the absorbing particulate organic matter (C_{POM})

$$C_{i,\text{POM}} = C_{i,\text{tot}} \left(1 + \frac{C_i^*}{C_{\text{POM}}} \right)^{-1}.$$ (1)

The effective saturation concentration of a compound can be expressed in terms of its vapor pressure (p_i^0), activity in the POM phase, and temperature (T)

$$C_i^* = \frac{p_i^0 \zeta_i \text{MW}_{\text{POM}}}{RT},$$ (2)

where MW_{POM} is the average molecular weight of the absorbing phase, ζ_i is the activity coefficient of the compound in that phase, and R is the gas constant. Most of the uncertainty in estimates of atmospherically relevant C_i^* is due to uncertainty in p_i^0 and ζ_i, because uncertainty in these variables can exceed a factor of 10 (e.g., p_i^0 estimates for hopanes and other cyclic, branched alkanes, or ζ_i of large hydrocarbons in polar organic solvents). Although there is obviously uncertainty in ambient MW_{POM} (and to a lesser extent, T), it will be secondary in terms of its impact on the theoretical value of C_i^*.

The fraction of a compound in the particle phase (f_{part}) depends on C_i^*

$$f_{i,\text{part}} = \frac{C_{i,\text{POM}}}{C_{i,\text{tot}}} = \frac{1}{1 + C_{i,\text{amb}}^*/C_{\text{POM}}}.$$ (3)

Neglecting the change in C_{POM} with mild heating, the fraction lost from the particle phase at a heated temperature (T_{heat}) relative to ambient (T_{amb}) can be expressed in terms of the increase in C_i^* with T

$$f_{i,\text{lost}} = 1 - \left(1 + \frac{C_{i,\text{amb}}^*}{C_{\text{POM}}} \right) \Big/ \left(1 + \frac{C_{i,\text{heat}}^*}{C_{\text{POM}}} \right).$$ (4)

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By inserting the definition of C_i^* Eq. (2) into Eq. (5), $f_{i,\text{lost}}$ can be expressed in terms of the physiochemical properties of compound i, T, and the concentration and average MW of the absorbing phase:

$$f_{i,\text{lost}} = 1 - \left(1 + \frac{p_{\text{amb}}^o \zeta_{i,\text{amb}} MW_{\text{POM}}}{RT_{\text{amb}} C_{\text{POM}}}\right) \Big/ \left(1 + \frac{p_{\text{heat}}^o \zeta_{i,\text{heat}} MW_{\text{POM}}}{RT_{\text{heat}} C_{\text{POM}}}\right). \tag{5}$$

5 Note that $f_{i,\text{lost}}$ is independent of $C_{i,\text{tot}}$, which is unknown in this study because gas-phase concentrations were not measured.

The above equations indicate that the volatility of a compound is related to the activity of that compound in its absorbing phase. If $\zeta_i > 1$, as would be expected for, e.g., a non-polar solute in a polar solvent, this would be reflected in a larger C^* for the com-
10 pound. As a consequence, the compound will exhibit greater volatility. Within a group of homologous compounds (e.g., the n-alkanes), f_{lost} will increase for all compounds as the temperature change driving evaporation increases; furthermore, the distribution of f_{lost} within the homologs (i.e., with molecular size) will shift as the composition of the absorbent changes (Fig. 1). Previous authors have reported that non-unity activity
15 coefficients are required to satisfactory model gas-particle partitioning of larger hydrocarbons in wood burning aerosol and secondary organic aerosol formed from α-pinene oxidation in smog chambers, while the assumption of solution ideality is satisfactory for these hydrocarbons in diesel exhaust (Jang et al., 1997). It is not known, however, which of these model aerosols best represents the absorbing phase(s) present in the
20 atmosphere. We calculate values of ζ_i using a modified version of UNIFAC (Gmehling et al., 1993), a group contribution activity coefficient model (Fredenslund et al., 1975). This version accounts for differences in molecular size between solvent and solute, and also performs relatively well for polar organic solvents. Along with experimental values for all compounds, we report theoretical f_{lost} for the n-alkanes because their vapor
25 pressures as a function of temperature are well-known (Lemmon and Goodwin, 2000). Therefore the n-alkanes can be used as a probe of absorbent composition through its effect on solute activity (manifested as n-alkane volatility).

3 Experimental

3.1 Field sites

The San Joaquin Valley (SJV), CA, experiences some of the highest airborne PM concentrations in the United States, especially in the winter when elevated temperature inversions create stagnation events lasting more than a week. Numerous source apportionment studies have been carried out in the SJV over the past decades (Chow et al., 1992, 2007; Magliano et al., 1999; Schauer and Cass, 2000; Rinehart et al., 2006; Chen et al., 2007; Kleeman et al., 2009). Earlier efforts apportioned the sources of PM_{10} (Chow et al., 1992), while more recent studies have focused on finer particles. All studies suggest a more regionally elevated secondary ammonium nitrate (AN) and/or organic aerosol in contrast to primary organic aerosols which show more spatial variability. Magliano et al. (1999) found that urban winter SJV $PM_{2.5}$ came primarily from mobile sources, burning, AN, and at times "excess OC," assumed to comprise secondary OC as well as unaccounted primary sources. Rural winter $PM_{2.5}$ was dominated by AN. Schauer and Cass (2000) used organic molecular markers in a chemical mass balance (CMB) model to determine that primary emissions account for 79% of urban $PM_{2.5}$ but less than 10% of $PM_{2.5}$ from a rural site in the SJV. Chow et al. (2007) found that inclusion of organic molecular markers in CMB analysis of Fresno (SJV) samples improved distinction between gasoline and diesel emissions, and precision of cooking emission estimates.

In the present study, ambient $PM_{1.8}$ samples were collected in Fresno in a mixed residential/commercial neighborhood (∼400 m from CA Hwy. 41) during the summer of 2006 and winter of 2007, and at a rural agricultural research station (∼100 km SW of Fresno and ∼10 km SW of Interstate 5) during the summer of 2007 and winter of 2008. Each sample was collected between the hours of ∼9 a.m. to ∼3 p.m. over five consecutive days in conjunction with heath effect studies whose results will be published elsewhere. Two sample pairs were collected in each season at both locations for a total of 16 samples (8 heated and 8 ambient). Ambient temperatures during the

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experiments ranged from 301 ± 5 K in summer to 287 ± 4 K in winter. Relative humidity (RH) also varied seasonally, from $34 \pm 9\%$ in summer to $60 \pm 13\%$ in winter. Bulk $PM_{1.8}$ filter samples were collected using Reference Ambient Air Samplers (RAAS) (Andersen Instruments) on pre-fired quartz filters ($D=45$ mm). Three separate RAAS

5   samplers were operated simultaneously, each with an "ambient" leg and a "heated" leg wrapped in electrical resistance heating tape. Temperature was monitored just downstream of the filter in the heated leg, and the average temperature increases in the heated legs of two co-located samplers were 9.6 ± 2.1 and 8.2 ± 2.7 K (quoted variation is 1σ). We used a 10 K temperature increase in all calculations, and results are

10 similar if either an 8 or a 12 K increase are used (Fig. 1). Identical downstream quartz back-up filters were subtracted from the front filters to correct for gas-phase adsorption artefacts.

3.2   Analyses

Organic carbon (OC) and elemental carbon (EC) were quantified at the University of

15 California-Davis with a Sunset Laboratory OC/EC Analyzer using the NIOSH 5040 thermo-optical method and sucrose as a calibration standard. Organic molecular markers were extracted by sonicating filters in dichloromethane followed by analysis using gas chromatography-mass spectrometry at the University of Wisconsin-Madison. The measured compounds included levoglucosan, cholesterol, 23 polycyclic aromatic hy-

20 drocarbons (PAHs), 16 hopanes/steranes, and 23 alkanes, including norpristane, pristane, phytane, and *n*-alkanes with carbon numbers from 17 to 36. Trimethylsyl (TMS) derivatives of levoglucosan and cholesterol were analyzed. Field filter blanks were analyzed alongside all samples and average blank values were subtracted from all results. Backup filter values were subtracted from front filter values to correct for adsorption of

25 gas-phase compounds onto the filter media.

4   Results

EC concentrations were slightly greater and more variable in the winter ($0.73 \pm 0.28\,\mu g\,m^{-3}$) than in the summer ($0.65 \pm 0.17\,\mu g\,m^{-3}$). The quoted uncertainty for these concentrations is 1σ of the measured variation of concentrations across
5 events. This trend reflects the increased emissions associated with heating and the formation of shallow inversion layers, which promotes higher PM concentrations, during the winter. This PM accumulation is counterbalanced with the increased frequency of precipitation events during the winter, which tend to reduce concentrations. Seasonal patterns for OC concentrations (winter: $3.9 \pm 1.3\,\mu g\,m^{-3}$ vs. summer: $3.7 \pm 0.8\,\mu g\,m^{-3}$)
10 matched the EC trends suggesting that anthropogenic sources contribute strongly to OC concentrations. Concentrations were greater at the urban site than the rural site for both [EC] ($0.72 \pm 0.27\,\mu g\,m^{-3}$ vs. $0.62 \pm 0.13\,\mu g\,m^{-3}$) and [OC] ($3.9 \pm 1.1\,\mu g\,m^{-3}$ vs. $3.3 \pm 1.1\,\mu g\,m^{-3}$).

The sum of detected n-alkane concentrations (C_{19}–C_{36}) was nearly five times greater
15 in summer ($28 \pm 44\,ng\,m^{-3}$) than in winter ($5.7 \pm 3.2\,ng\,m^{-3}$). Likewise, the sum of the concentrations for the 15 hopanes and steranes that were detected was over five times greater during the summer ($0.54 \pm 0.64\,ng\,m^{-3}$) than in winter ($0.10 \pm 0.08\,ng\,m^{-3}$). All three classes of alkanes were more abundant at the urban site (Fig. 2a,c,e); however, the difference between the two sites was less prominent when their concen-
20 trations were normalized to [EC] (Fig. 2b,d,f). The two most abundant hopanes, 17β(H),21α(H),30-norhopane and 17α(H),21β(H)-hopane (average concentrations of 77 and $64\,pg\,m^{-3}$, respectively) were well correlated ($r^2 = 0.98$).

Out of the 23 PAHs that were measured, six were not detected, including three-ring molecules such as phenanthrene and anthracene. The lightest PAHs detected
25 had MWs of $202\,g\,mol^{-1}$ (fluoranthene and pyrene). In general, individual [PAH]s were greater in the winter (Fig. 2g), in contrast to the alkanes, and this was also true of [PAH]/[EC] ratios (Fig. 2h). The total PAH concentration ([PAH]$_{tot}$) was also greater in the winter than in summer, but summer variability was greater (winter:

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0.20 ± 0.09 ng m^{-3}, summer: 0.17 ± 0.16 ng m^{-3}). The quoted summer mean and standard deviation of [PAH]$_{tot}$ is dominated by a single anomalous ambient [retene] measurement in Fresno summertime of 0.31 ng m^{-3}. Retene was not detected in any of the other seven summer samples, nor was it detected in the co-located heated samples. If retene is omitted from the analyses, summertime [PAH]$_{tot}$ drops to 0.13 ± 0.08 ng m^{-3}.

Levoglucosan concentrations had seasonal trends similar to EC, OC, and PAHs with higher concentrations and greater variability in the winter than the summer (43 ± 18 vs. 7 ± 8 pg m^{-3}). Winter concentrations would likely have been much higher if samples had been collected at night when home heating with wood combustion is common in the SJV (Kleeman et al., 2008). Cholesterol concentrations were lower than any other compounds reported here, averaging only 1.0 ± 0.9 pg m^{-3} in the summer and 0.3 ± 0.3 pg m^{-3} in the winter. Thus the seasonal patterns of cholesterol were similar to those for hopanes/steranes and *n*-alkanes.

Figure 3 illustrates the fraction of each chemical species lost from the particle phase in the sample that was heated ∼10 K above the ambient temperature. Neither EC or OC concentrations had a statistically significant response to heating: [EC]$_{heat}$/[EC]$_{amb}$ was 0.95 ± 0.05, and [OC]$_{heat}$/[OC]$_{amb}$ was 1.02 ± 0.04 (quoted uncertainty for heated:ambient ratios is the 95% confidence interval, see Fig. 3a,b). Heating caused only a slight volatilization of PAHs (excluding retene) in both seasons (winter [PAH]$_{heat}$/[PAH]$_{amb}$=0.87±0.06, summer [PAH]$_{heat}$/[PAH]$_{amb}$=0.95±0.09) despite the fact that the lighter PAHs considered in the analysis have saturation concentrations that make them semi-volatile according to absorptive partitioning theory. Retene was the exception to this trend, with almost complete loss of retene for a single heated/ unheated sample pair (Fig. 3c). Concentrations of the unsaturated hydrocarbons including hopanes/steranes and *n*-alkanes decreased significantly with mild heating (Fig. 3d,e), with the exception of *n*-alkanes in summer at the rural site. The volatility of the alkanes was greater at the urban site during the summer (52% loss for hopane/steranes and 84% loss for *n*-alkanes) than in the winter (40% loss and 38% loss, respectively). In contrast, the mass of *n*-alkanes in the rural samples was actually

15% greater in the heated leg (Fig. 3e) during summer. However, if the backup filter subtraction is neglected, the fraction lost to heating was 18% at Westside and 77% at Fresno. This can be seen in a plot of both front and backup filter concentrations vs. carbon number (Fig. 4), which shows that at the rural site in summer, front and backup filter *n*-alkane concentrations were approximately equal, while the backup filter concentrations were reduced in the heated leg. The OC on backup filters contains gas-phase compounds that adsorb onto the quartz, and these results therefore suggest that adsorption of rural VOCs is more reversible than for urban VOCs, which is consistent with more strongly-adsorbing compounds emitted in Fresno being removed from the atmosphere before reaching the rural site. Levoglucosan concentrations were reduced by 10% with heating, i.e., their apparent volatility was similar to the PAHs. Likewise, cholesterol concentrations did not experience a statistically significant change in response to heating (Fig. 3f).

5   Discussion

Both the seasonal patterns of molecular marker concentrations and their volatility behavior with mild heating suggest different partitioning mechanisms for PAHs on one hand, and hopane/steranes and *n*-alkanes on the other. Specifically, the low volatility and higher wintertime concentrations exhibited by the PAHs suggest that absorptive partitioning may only be a minor contributor to particle-phase concentrations. Previous studies have concluded that partitioning of PAHs into urban aerosols as a function of temperature is best explained by an adsorption mechanism (Yamasaki et al., 1982), and adsorption onto soot might dominate gas-particle partitioning of PAHs into of urban aerosols (Dachs and Eisenreich, 2000). A review of a broader range of ambient aerosols found that soot adsorption was likely responsible for particle-phase [PAH]s greater than those calculated for OA absorption (Lohmann and Lammel, 2004). We found that PAH volatility was lower on average at Fresno (10 ± 8%) than at Westside (20 ± 8%), but was roughly equivalent in summer (11 ± 11%) and winter (13 ± 6%).

This non-volatile behavior is consistent with adsorption of most of the particle-phase PAHs onto soot, and also with a greater number of surface sites per unit mass of soot near sources (i.e., at the urban site). According to the results of Yamaski et al. (1982), a change in T from 301 to 313 K would increase the adsorptive partitioning coefficient (defined analogously to C^*) of fluoranthene, pyrene, and benzopyrene by 76%, 70%, and 86%, respectively. In contrast, the calculated increase in C^* for the n-alkanes associated with the same temperature increase is 470% for eicosane (C_{20}) and increases to 1600% for hexatricontane (C_{36}). Our results are consistent with a greater sensitivity to temperature of the absorption vs. the adsorption partitioning coefficient.

Given the volatility exhibited by the n-alkanes and hopanes/steranes, it is somewhat surprising that particle-phase concentrations of these compounds were greater in summer than winter by a factor of five. Since the emissions sources of these compounds do not undergo five-fold increases in summer vs. winter, it is expected that seasonal changes to the absorbing particulate matter must be responsible for the differences in particle-phase concentrations. Closer inspection of the data reveals that n-alkanes and hopanes/steranes were most volatile during the summer at the urban site (Fig. 5), which would result from a greater capacity of the fresh urban particulate organic phase to absorb large hydrocarbons. The seasonal difference could be related to the lower daytime RH in the SJV summer, which would reduce the particle-phase water content and might therefore promote higher concentrations of the absorbing organic (non-aqueous) phase. This summertime increase in C_{POM} would result in a roughly proportional increase in the particle-phase concentrations of n-alkanes and hopanes/steranes. The increase in humidity during wintertime may promote the sorption of organic material onto an aqueous phase, which might (like soot) be less sensitive to temperature than is absorptive partitioning. Furthermore, organic matter may absorb into or adsorb onto an aqueous phase, which would reduce the size of the organic phase available to absorb non-polar organic compounds. To summarize, our results suggest that particle-phase concentrations of large hydrocarbons are limited by the abundance of a relatively non-polar organic phase.

During the summer, the temperature-induced volatility of the *n*-alkanes increased with carbon number in the range 21–28, and then decreased with carbon number from 28–35 (Fig. 6a). This pattern, particularly the decrease in volatility at higher carbon number, is consistent with group-contribution estimates of ζ as a function of MW. How-

5 ever, f_{lost} approaches zero at a larger carbon number than predicted assuming the *n*-alkanes form an ideal solution in their absorbent. Relaxing the assumption of ideality and modelling the absorbent as a mixture of 40 compounds, including carbonyl compounds observed in vehicular emissions (Jakober et al., 2008), as a surrogate for light-duty vehicle particulate emissions (Chen et al., 2010) results in only minor changes in

10 f_{lost} with carbon number, because the predicted activity coefficients are close to unity. We also modelled the absorbent using surrogate compounds picked to represent organic aerosol factors identified by positive matrix factorization of high-resolution aerosol mass spectrometer data collected in Mexico City (Aiken et al., 2009). Specifically, Aiken et al. (2009) isolated a "hydrocarbon organic aerosol" (HOA) that had O:C=0.16 and

15 H:C=1.84, and an "oxygenated organic aerosol" that had O:C=0.60 and H:C=1.47. We use 12-hydroxy-dodecanal (O:C=0.17, H:C=1.83, MW=198) and 5-oxo-pentanoic acid (O:C=0.60, H:C=1.60, MW=116) as surrogates for HOA and OOA, respectively. Other highly oxygenated surrogate organic phases, such as a model fulvic acid compound (Buffle et al., 1977) and glyoxal oligomers, produced results similar to OOA.

20 Volatility was reduced in the winter for the *n*-alkanes (Fig. 6b), which could be due to the increased importance of other partitioning mechanisms (e.g., adsorptive) during times when the aerosol water content is higher. If, at elevated RH, the non-aqueous phase exists as a "core" surrounded by an aqueous phase, this latter phase could act as a barrier to mass transfer which might explain the reduced winter volatility, as long

25 as this phase was not completely volatilized by a $\sim$10 K increase in temperature. Such a barrier to mass transfer could explain the reduced reactivity of hopanes/steranes observed at high RH in smog chamber experiments (Weitkamp et al., 2008), if their reactivity is coupled to their volatility. Still, a decrease in volatility was evident in larger *n*-alkanes (with carbon numbers above 29) during the winter, suggesting that, as with

the summer samples, the absorbing phase was about as polar as OOA.

The volatility of *n*-alkanes was substantial in the urban summer; in sharp contrast, [*n*-alkane]$_{heat}$/[*n*-alkane]$_{amb}$ ratios were typically greater than one in the rural summer. This was primarily due to reduced [*n*-alkane] on the heated leg backup filter, which traps gas-phase compounds mainly by adsorption onto the surface of quartz fibres. When concentrations only on the front filter are considered, rural summer *n*-alkane concentrations were slightly greater in the ambient leg than in the heated leg (Fig. 5a). PM analysis by aerosol mass spectrometry has indicated that while urban organic aerosols are a mixture of a "hydrocarbon-like" and "oxygenated" organic aerosol, background/rural sites tend to be dominated by oxygenated organic aerosol (Zhang et al., 2007; Aiken et al., 2009). It therefore seems likely that the lower rural f_{lost} of *n*-alkanes is due to a more oxygenated phase into which larger, unsaturated hydrocarbons cannot absorb efficiently. For example, in an organic phase represented by succinic acid (blue lines on Fig. 1a), C^* is greater than $10\,\mu g\,m^{-3}$ for all *n*-alkanes studied, and greater than $100\,\mu g\,m^{-3}$ for all *n*-alkanes with carbon number less than 33. Thus, under normal ambient conditions, nearly all of the *n*-alkanes will remain in the gas phase rather than absorb into a succinic acid POM phase. The *n*-alkanes present in the PM must therefore partition via a different mechanism (e.g., adsorption to soot), one unaffected by a 10 K increase in temperature.

Volatility for hopanes/steranes was also greater in the summer vs. winter (f_{lost}=58% vs. f_{lost}=36%), matching the trends exhibited by *n*-alkanes. The summertime value suggests that these compounds have similar volatility as C$_{29}$–C$_{32}$ *n*-alkanes under atmospherically-relevant conditions. The hopanes and steranes quantified had carbon numbers ranging from 27 to 32, which implies that hopanes/steranes are about equally or only slightly less volatile than *n*-alkanes with similar MW. The summertime f_{lost} for hopanes peaked at a carbon number or 30 (Fig. 4), again consistent with an absorbing phase about as polar at succinic acid. Like the *n*-alkanes, hopane/steranes were less volatile in the winter, and even less so at the rural summer site. Overall, the similarity between hopane/steranes and *n*-alkanes suggests that hopanes/steranes have

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saturation concentrations on the order of 0.1–10 $\mu g\,m^{-3}$, depending on the chemical identity of the absorbing phase, and should generally be considered semi-volatile.

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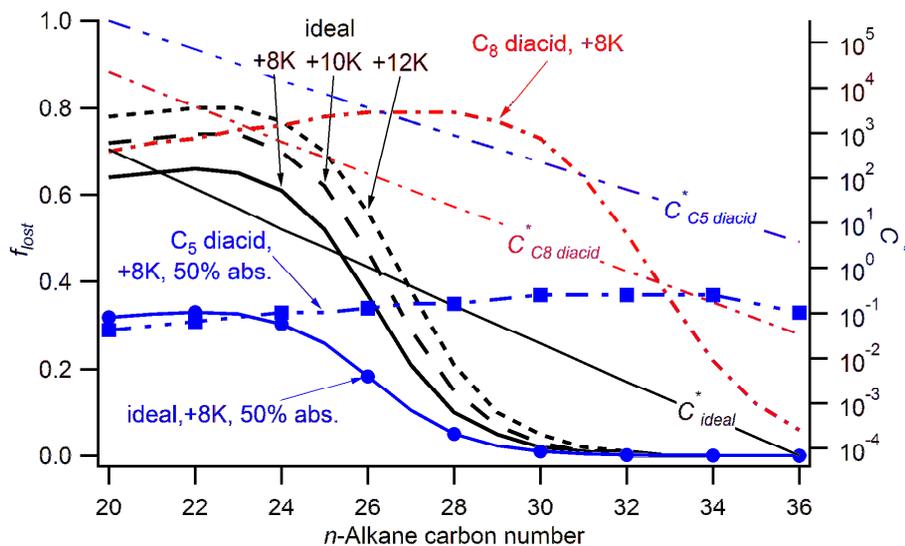
Fig. 1. Theoretical volatility of n-alkanes when $C_{POM}=4\,\mu g\,m^{-3}$, expressed as f_{lost} (thick curves, left axis) and C^* (thin lines, right axis) vs. carbon number. If the alkanes are assumed to form an ideal solution with the absorbing phase, $C^* \sim C_{POM}$ for a C_{24} alkane, and thus this is where f_{lost} is greatest. If the heating is increased, the curve shifts upwards (to higher f_{lost}), but only slightly to the right (higher carbon number). If the absorbent is assumed to be a C_8 diacid, the enhanced activity of the alkanes results in much greater C^* and the curve shifts primarily to the right. If only 50% of the particle-phase alkanes are absorbed and the rest are assumed to be non-volatile, f_{lost} is reduced accordingly (lines with symbols). For a relatively polar absorbent (e.g., a C_5 diacid), alkane C^*s are large enough that partitioning is negligible under typical atmospheric COA, and thus variation in f_{lost} with carbon number from 20 to 36 is minor.
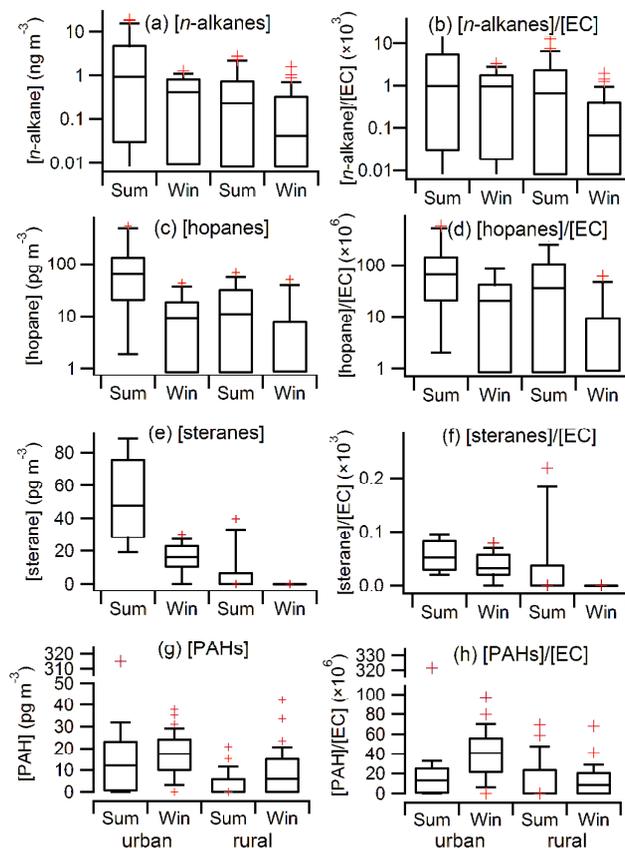
Fig. 2. Box and whisker plots of the concentrations of all compounds measured at ambient temperatures during the current study, as well as concentrations normalized to [EC]. **(a)** absolute and **(b)** normalized [*n*-alkanes]; **(c)** absolute and **(d)** normalized [hopanes]; **(e)** absolute and **(f)** normalized [steranes]; **(g)** absolute and **(h)** normalized [PAHs].
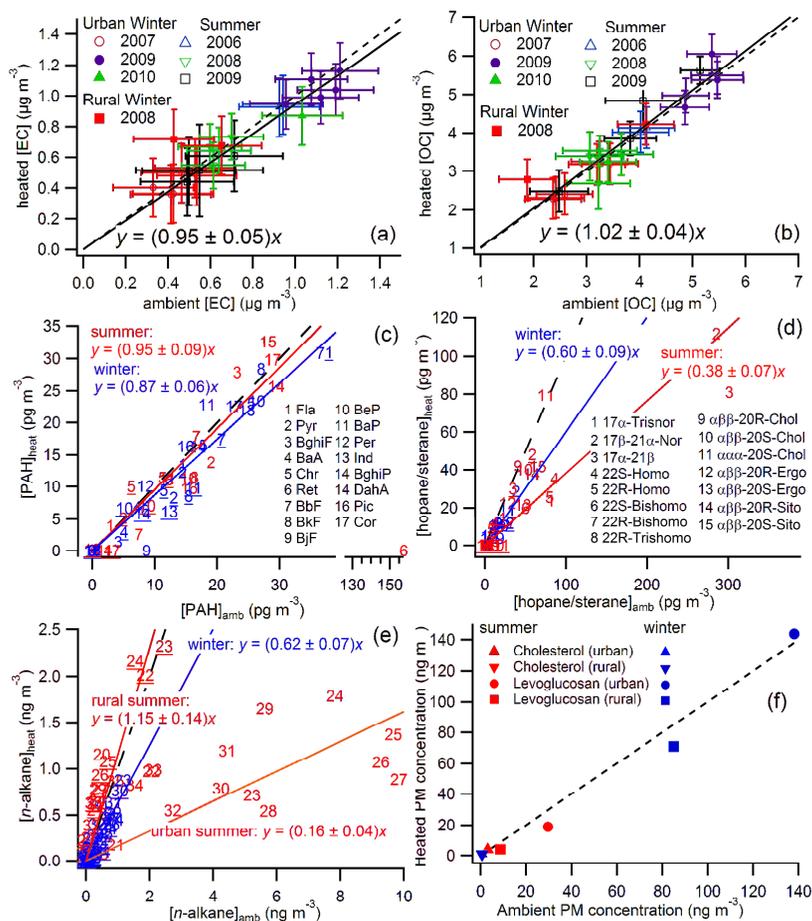
Fig. 3. Heated vs. ambient (unheated) concentrations. **(a)** EC, **(b)** OC, **(c)** PAHs, **(d)** hopanes and steranes, **(e)** *n*-alkanes, **(f)** cholesterol and levoglucosan.

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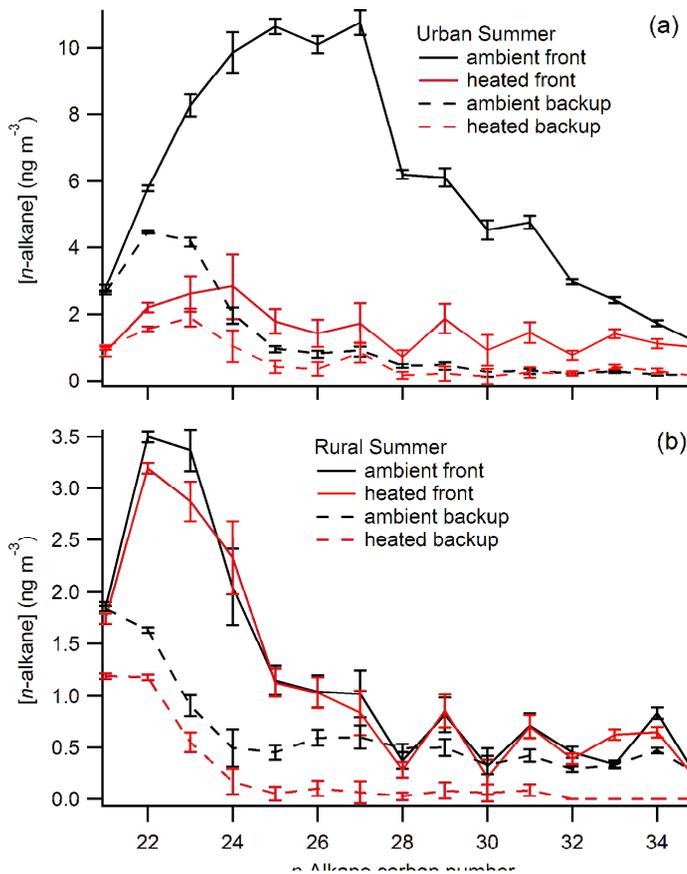
Fig. 4. Concentrations of *n*-alkanes as a function of carbon number. Results from both front (solid lines) and backup (dashed lines) filter are depicted. Color indicates sample leg, with black representing the ambient leg and red representing the heated leg. **(a)** Urban summer, **(b)** rural summer.
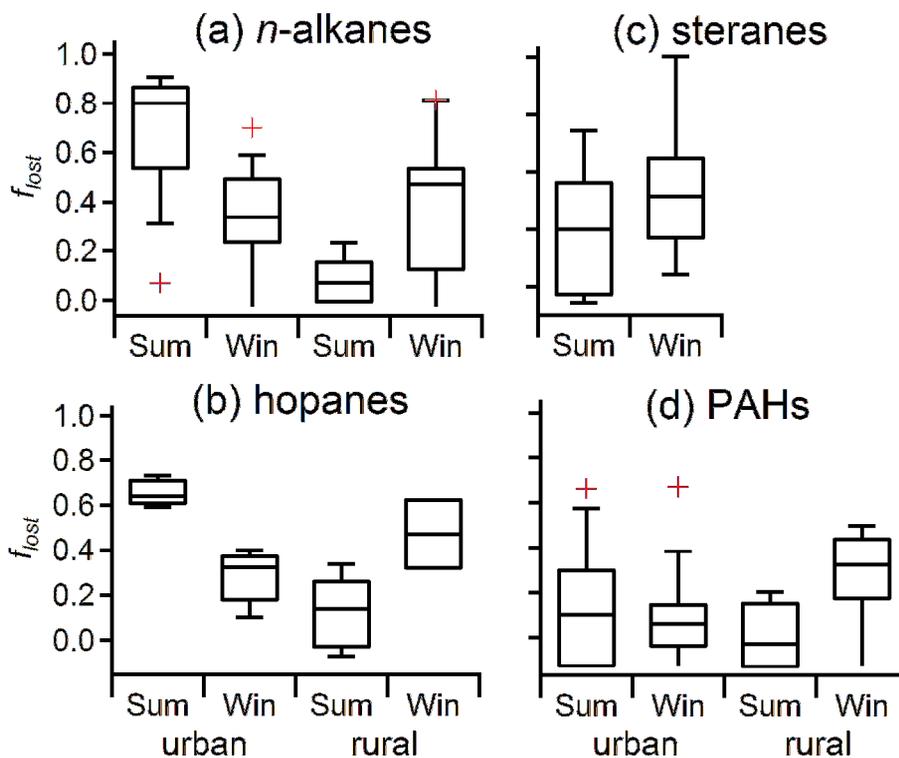
Fig. 5. Box and whisker plots depicting the fraction lost to mild heating (f_{lost}) of various compound classes, separated by season and location. **(a)** n-alkanes, **(b)** hopanes, **(c)** steranes (which were not detected at the rural site), **(d)** PAHs.
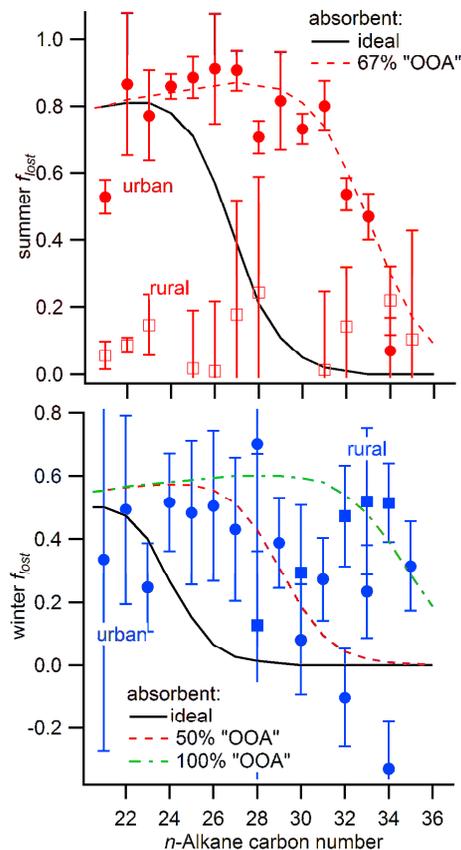
Fig. 6. Observed values of *n*-alkane f_{lost} (circles are urban, squares are rural) as a function of carbon number, along with that predicted using a group-contribution activity coefficient model with various assumptions regarding the composition of the absorbing phase (lines). **(a)** Summer results. Rural values are depicted as open symbols to indicate that backup-filter subtraction was not performed. **(b)** Winter results.

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