

Effect of Vaporizer Temperature on Ambient Non-Refractory Submicron Aerosol Composition and Mass Spectra Measured by the Aerosol Mass Spectrometer

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Abstract

Aerodyne Aerosol Mass Spectrometers (AMS) are routinely operated with a constant vaporizer temperature (T_{vap}) of 600°C in order to facilitate quantitative detection of non-refractory submicron (NR-PM₁) species. By analogy with other thermal desorption instruments, systematically varying T_{vap} may provide additional information regarding NR-PM₁ chemical composition and relative volatility, and was explored during two ambient studies. The performance of the AMS generally and the functional integrity of the vaporizer were not negatively impacted during vaporizer temperature cycling (VTC) periods. NR-PM₁ species signals change substantially as T_{vap} decreases with that change being consistent with previous relative volatility measurements: large decreases in lower volatility components (e.g., sulfate, organic aerosol (OA)) with little, if any, decrease in higher volatility components (e.g., nitrate, ammonium) as T_{vap} decreases. At T_{vap} < 600°C, slower evaporation was observed as a shift in particle time-of-flight distributions and an increase in “particle beam blocked” (background) concentrations. Some chemically-reduced (i.e., C_xH_y⁺) OA ions at higher m/z are enhanced at lower T_{vap} , indicating that this method may improve the analysis of some chemically reduced OA systems. The OA spectra changes dramatically with T_{vap} , however the observed trends cannot easily be interpreted to derive volatility information. Reducing T_{vap} increases the relative O:C and CO₂⁺, contrary to what is expected from measured volatility. This is interpreted as continuing decomposition of low volatility species that decreases more slowly (as T_{vap} decreases) than does the evaporation of reduced species. The reactive vaporizer surface and the inability to reach T_{vap} much below 200°C of the standard AMS limit the ability of this method to study the volatility of oxidized OA species.

1. Introduction

The Aerodyne Aerosol Mass Spectrometers (AMS) (Canagaratna, et al. 2007) as well as the recently developed Aerosol Chemical Speciation Monitor (ACSM) (Ng, et al. 2011) are widely used to monitor the chemical composition of ambient and laboratory-generated non-refractory submicron (NR-PM₁) aerosols in real time. The AMS and ACSM consists of three main parts: an aerodynamic lens, a high-vacuum particle time-of-flight chamber, and a chemical analyzer based on thermal desorption and mass spectrometry. Particles sampled into the instrument are first collimated into a tight, non-divergent particle beam as they pass through a series of aerodynamic lenses (Zhang, et al. 2004). Upon exiting the lens system, particles gain a size-dependent velocity at which they traverse the particle time-of-flight (PToF) chamber and eventually collide, under high-vacuum conditions, with a resistively heated vaporizer located after the end of the PToF chamber. The outcome of this collision, specifically whether ions of the particle-associated species reach the detector and generate a signal, depends on their tendency to vaporize at the standard AMS vaporizer temperature (T_{vap}) of 600°C. “Non-refractory” components are empirically defined as those that vaporize quickly under these conditions, with the resulting vapor plume undergoing ionization by electron impact and mass analysis by the spectrometer. A fraction of ambient particles as well as laboratory particles for some species, however, are known to bounce from the vaporizer without significant vaporization. The AMS collection efficiency (CE) is used to correct for this effect (Matthew et al., 2008; Middlebrook et al., 2012; Docherty et al., 2012).

Several thermal desorption techniques have been demonstrated to exploit different evaporation rates among species to qualitatively and/or quantitatively characterize the volatility of aerosol components. The thermal desorption particle beam mass spectrometer (TDPBMS) accumulates aerosol particles on a cryo-cooled surface which is slowly heated to 150°C thereby separating individual compounds based on their different evaporation rates under vacuum (Tobias and Ziemann 1999), and allows for the quantitative measurement of individual compound vapor pressures (Chattopadhyay, et al. 2001, Chattopadhyay and Ziemann 2005). Thermodenuder (TD) systems consisting of a heated tube to evaporate particle mass have a long history in atmospheric research and rely on this same basic principle. TD systems have recently been interfaced with both the TDPBMS (Faulhaber, et al. 2009) and the AMS (Huffman, et al. 2009a,b) to explore the volatility of laboratory-generated and ambient aerosols. Faulhaber, et al. (2009) and Cappa and Jimenez (2010) have used TD data to derive volatility distributions of different organic aerosol types. Other systems with similar functionality have been demonstrated by Yatavelli, et al. (2012), and Lopez-Hilfiker, et al. (2014). Salcedo, et al. (2010, 2012) provided evidence that differential evaporation rates of various aerosol components within the AMS (with T_{vap} =600°C) can exist and be used to enhance our understanding of aerosol chemical composition. Although it is possible to vary the AMS T_{vap} rapidly,

the potential of using this variation to obtain volatility information similar to that provided by other thermal desorption measurements and to differentiate among NR-PM₁ species has not been explored to our knowledge.

Rapid T_{vap} cycling as a means of obtaining additional information regarding NR-PM₁ composition and component volatility is attractive given the widespread availability of AMS instruments worldwide and the fact that it can be accomplished without the need for additional instrumentation outside of the AMS itself. Here, we sampled ambient aerosol during two field experiments in urban (Study of Organic Aerosols at Riverside, SOAR-2005) and forested (Biosphere Effects on Aerosols and Photochemistry Experiment, BEARPEX-2007) sites while systematically and rapidly changing T_{vap} every ~30 min., in order to explore the impact of $T_{vap}<600^{\circ}\text{C}$ on NR-PM₁ apparent composition and mass spectra, and whether this experiment can provide information on the relative volatility of various NR-PM₁ components.

2. Experimental

2.1 Vaporizer temperature control

The AMS vaporizer is a cartridge heater (Heatwave Labs, <http://www.cathode.com/>) with an inverted cone porous sintered tungsten tip that is heated by passing DC current over an internal ~3 Ohm resistor. DC power supplied to the vaporizer and T_{vap} can be controlled either manually, via the AMS electronics front panel, or remotely, via computer control, by interfacing a control voltage output from a digital-to-analog converter. Under standard AMS sampling protocols, T_{vap} is manually set to 600°C with a constant output (typically 3.6V; 1A) using the AMS electronics front panel.

2.2 Field Experiments: Automated vaporizer temperature cycling (VTC)

In order to systematically explore its impact on measured NR-PM₁ composition, T_{vap} was systematically varied during ambient sampling using a variable temperature control (VTC) software module written using Microsoft Visual Basic 6. At the core of the VTC module is a proportional-integral-derivative (PID) controller that uses the vaporizer temperature (T_{vap}) to monitor and adjust the voltage output to the vaporizer at a rate of 10 Hz in order to closely follow a target T_{vap} set by the software. The VTC module not only allows a constant T_{vap} to be continuously maintained but also provides a means by which T_{vap} can be rapidly increased with little overshoot. The VTC module was also designed to continuously cycle through a T_{vap} profile consisting of a number of temperature steps with both T_{vap} and the duration of each step preset by the user. T_{vap} is measured by a thermocouple mounted near the back of the AMS vaporizer and is displayed on the electronics box. T_{vap} was input directly into the VTC PID controller without additional calibration. According to manufacturer specifications, a properly functioning vaporizer requires approximately 3.0-3.5 W (~1.0A) to maintain a $T_{vap}=600^{\circ}\text{C}$ and additional steps to calibrate T_{vap} are recommended only in the event that excess

power consumption is required to maintain the standard operating temperature. During SOAR-2005 and BEARPEX-2007, the vaporizer power requirements were within this specified range and no additional steps were taken to determine whether there was any substantial deviation between measured and actual T_{vap} .

The VTC system was operated on two different AMS instruments for the first time during SOAR-2005 (15 July–15 August, 2005): a high-resolution time-of-flight AMS (HR-AMS, VTC operative between 10–13 August) and a compact time-of-flight AMS (C-AMS, VTC operative between 3–13 August). Details regarding HR-AMS and C-AMS operation during SOAR-2005 and the broader campaign objectives and results are presented elsewhere (Docherty, et al. 2011). The T_{vap} control profile (i.e., the target T_{vap} (duration) of each step) was identical for both instruments: 200°C (15 min); 350°C (5 min); 450°C (5 min), and; 600°C (5 min). Although $T_{vap}>600^{\circ}\text{C}$ are possible with the standard AMS vaporizer, they can lead to premature vaporizer failure and were not explored in this work. Both instruments were configured to operate with a file save interval of one minute in order to capture composition changes in greater detail and VTC and AMS data acquisition software were run on the same system computer in order to synchronize temperature transitions with the data acquisition time grid. In mass spectrum (MS) mode the particle beam chopper alternated between “particle beam open” (open) and “particle beam closed” (closed) every five seconds.

Profiles of average T_{vap} throughout the HR- and C-AMS VTC cycling periods during SOAR-2005 are shown in Figure 1a. Individual data points represent average T_{vap} at each minute of the VTC cycle across all cycles while error bars represent twice the corresponding standard deviation. Both T_{vap} profiles are quite similar, with small differences likely due to differences in vaporizer geometry or thermocouple placement. Overall the 600°C→200°C transition is the slowest requiring 5-10 min due to the limited rate of passive heat loss from the vaporizer. In contrast, increasing T_{vap} transitions occur rapidly with little, if any, significant overshoot and a stable higher T_{vap} is obtained in <2 min. It is important to note that, although each instrument collected data at each minute of the VTC cycle data acquired during T_{vap} transitions were not considered in the analyses below.

For the BEARPEX-2007 study, the VTC software was modified to alternate between the T_{vap} stepping protocol described above and a linear T_{vap} ramp from 600°C→200°C. This version was operated on an HR-AMS between 7 and 13 September, 2007, during which time HR-AMS sampling alternated between VTC sampling and eddy covariance flux measurement periods (Farmer, et al. 2013). As was the case during SOAR-2005, the HR-AMS was operated with a data saving frequency of one minute but a slightly modified control profile due to campaign specific time constraints: 200°C (9 min); 350°C (4 min); 450°C (4 min) and; 600°C (6 min). For the linear ramp, T_{vap} was decreased from 600°C to 200°C over a period of 13 min, held at 200°C for 3 min, and thereafter rapidly increased back to 600°C. Results from both protocols are shown in Fig. 1b. It is interesting to note that even the

200°C→600°C transition at the end of the ramp cycle again requires only <2 min to achieve stability. As was the case for SOAR-2005, the particle beam chopper alternated between open and closed phases every five seconds in MS mode.

3. Results and Discussion

3.1 Are Standard AMS Results affected by VTC operation?

The use of VTC to systematically vary T_{vap} provides an opportunity to evaluate the feasibility of long-term T_{vap} cycling in the AMS. Of particular concern is whether VTC sampling negatively impacts either the functional integrity of both the vaporizer and its power supply or the quantitative measurements of the AMS. During both SOAR-2005 and BEARPEX-2007, T_{vap} was cycled continuously for a period of several days to a few weeks with no detrimental change apparent in the function of the vaporizer or its power supply. VTC sampling also does not appear to impact the quantitative capacity of the AMS during $T_{vap}=600^{\circ}\text{C}$ sampling intervals. SOAR-2005 HR-AMS measurements showed a high level of agreement with those of collocated instruments, including a filter dynamics measurement system tapered element oscillating micro balance (FDMS-TEOM) (Docherty, et al. 2011) even during VTC sampling. HR-AMS total NR-PM₁ measured during both VTC operation when $T_{vap}=600^{\circ}\text{C}$ and standard (i.e., non-VTC, constant $T_{vap}=600^{\circ}\text{C}$) sampling periods are compared with corresponding FDMS-TEOM measurements in Figure S1. Apart from a slope greater than unity due to the different size cuts of the two instruments and the contribution from refractory material (Docherty, et al. 2011), data from the two periods is not substantially different. HR-AMS total NR-PM₁ measured during VTC operation (again only at $T_{vap}=600^{\circ}\text{C}$) is also compared with total NR-PM₁ from a collocated C-AMS (operating with a constant $T_{vap}=600^{\circ}\text{C}$) over the same interval in Fig. S1 and shows excellent agreement.

VTC parameters and NR-PM₁ species apparent concentrations from a 14 hr period during SOAR-2005 are shown in Figure 2. Ar⁺ signal and mass spectrometer parameters show little, if any, dependence on T_{vap} indicating that the operation of the AMS ionizer and mass spectrometer are not affected by the cycling on T_{vap} . Thus VTC operation does not cause a degradation of the performance of the AMS, and the periods with standard $T_{vap} = 600^{\circ}\text{C}$ can be used as standard ambient data without any corrections.

3.2 Changes in Detected NR-PM₁ Species with T_{vap}

Aerosol species signals show a clear dependence on T_{vap} that correlates with their previously reported volatilities (Huffman, et al. 2009). Relatively low volatility organic aerosol (OA) and sulfate (SO₄) concentrations exhibit substantial variation, while the variability of relatively high volatility nitrate (NO₃), ammonium (NH₄), and chloride (Cl) is far smaller. The majority of particle-associated NO₃ during SOAR-2005 is thought to arise from volatile ammonium nitrate (NH₄NO₃) (Docherty, et al. 2011,

Farmer, et al. 2010). Similarly, the majority of Chl in urban areas is thought to be contributed by volatile ammonium chloride (Salcedo, et al. 2006). As more of the NH_4 during this period is associated with NO_3 than SO_4 , its relative change with T_{vap} is also more similar to that of NO_3 . A similar plot from a different period of C-AMS sampling during SOAR-2005 is shown in Figure S2 and shows similar results. Thus VTC operation can provide some information on the relative volatility of different species.

Consistent trends are observed in PToF distributions, as shown in Figure 3 and S3. Detection in PToF mode requires evaporation in a few ms, compared to a few s in MS mode. Distributions of lower volatility species change dramatically as T_{vap} decreases. Most notably, the OA PToF distribution exhibits a profound decrease even over the $600^\circ\text{C} \rightarrow 450^\circ\text{C}$ transition while distributions of more volatile species such as NO_3 display little, if any, change until T_{vap} approaches the 200°C minimum. In addition to a decrease in overall amplitude of the PToF distributions, a small shift to larger apparent sizes is also observed in the distributions of many species, indicating slower vaporization of those species as T_{vap} decreases. These shifts tend to occur at a higher T_{vap} for lower volatility species and lower T_{vap} for higher volatility species. Shifts in OA and Chl are less apparent possibly due to the wider overall distribution and more complex composition in the case of OA and low concentrations in the case of Chl.

Difference (i.e., open minus closed) signals vs. time in a T_{vap} cycle are shown in Figure 4. The difference signals are consistent with Fig. 2-3, and also show that the signals follow T_{vap} with little delay. Interestingly MS and PToF SO_4 signals are consistent with the exception of $T_{\text{vap}} = 200^\circ\text{C}$. At this temperature, PToF concentrations are essentially zero while MS concentrations are about half 600°C values. This is likely due to the SO_4 vaporization timescale at the lowest T_{vap} becoming significantly longer than the ~ 10 ms available in PToF mode. A similar effect appears for OA which decreases by $\sim 80\%$ in PToF but only $\sim 50\%$ in MS mode between maximum and minimum T_{vap} . A lower fraction of OA evaporating at the lowest T_{vap} suggest an overall lower volatility relative to SO_4 , consistent with TD results (Huffman, et al. 2009). Analysis for the SOAR-2005 C-AMS data in Figure S4 shows very similar results. Importantly, the fragmentation of inorganic NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ (i.e., the relative ratio among major fragments) appears to change very little, if any, between maximum and minimum T_{vap} (ref. Figure S5).

3.3 Changes in Detected NR-PM₁ Background Species with T_{vap}

Background signals in the AMS are measured every 5-10 seconds using the closed mode, in order to remove them before the calculation of concentrations. Slowly evaporating species in the AMS, however, can increase background signals and that increase can be monitored in time and used to detect plumes of “semi-refractory” species such as lead sulfides (Salcedo, et al. 2010, 2012). Under typical operation conditions with $T_{\text{vap}} = 600^\circ\text{C}$, major NR-PM₁ species have only a small fraction of their particle signal appearing in the closed mode, typically $\sim 2\%$ for NH_4 and NO_3 and $\sim 18\%$ for SO_4 and

OA (see Fig. 4 & 8 of (Huffman, et al. 2009)). As T_{vap} and species evaporation rates are decreased, however, a larger fraction of the signal of NR-PM₁ species may appear in the closed spectrum.

Closed signals as a function of T_{vap} are also shown in Fig. 4. Overall, closed profiles are similar to difference profiles with concentrations decreasing with T_{vap} relative to 600°C. A notable difference is observed for each species at T_{vap} =200°C at which temperature closed concentrations increase relative to difference concentrations. This increase is most prominent for NO₃ and NH₄, concentrations which increase by ~25% and >50%, respectively, relative to T_{vap} =600°C. Given that NO₃ and NH₄ PToF distributions exhibit a slight shift to larger apparent sizes at this T_{vap} , the increase in closed concentrations is likely due to delayed vaporization that transfers mass from the open to the closed acquisition interval. Much smaller increases are observed for the lower volatility species SO₄ and OA at T_{vap} =200°C suggesting that the magnitude of the mass fraction appearing in the closed acquisition period due to delayed vaporization is proportional to volatility (i.e., large mass fractions appearing in closed for high volatility species and decreasing with decreased volatility).

Large spikes are observed in the closed profiles of both SO₄ and OA during increasing T_{vap} transitions indicating that at least a fraction of both species persists on the vaporizer surface at T_{vap} ≤450°C. This fraction, however, is relatively minor as spikes are observed only in the closed concentrations profile and the duration of these spikes is relatively short (<1 min) even at the lowest T_{vap} . I.e., the amount of signal observed during these short spikes is much smaller than what would be expected if all the missing signal suddenly appeared. Spikes are nearly absent from the closed profile of NO₃ indicating that little accumulation of relatively volatile species occurs.

A more likely cause of lower difference and closed concentrations at T_{vap} <600°C is bounce of a larger fraction of the particles from a cooler vaporizer surface. A substantial fraction of pure SO₄ (Matthew, et al. 2008) and highly oxidized chamber-generated OA (Docherty, et al. 2013) bounce from the AMS vaporizer at the standard T_{vap} and the fraction lost due to bounce should stay constant or increase with decreasing T_{vap} . Increased bounce from the vaporizer lowers difference concentrations as less mass remains on the vaporizer surface for a sufficient amount of time to allow for vaporization. It may also reduce closed concentrations (relative to T_{vap} =600°C) as less mass is available to be shifted to the closed interval through delayed vaporization. The degree to which bounce decreases closed concentrations, however, is complicated by the tendency of delayed vaporization to increase closed concentrations (relative to difference concentrations) as T_{vap} decreases. The competition between these two effects at different T_{vap} may lead to the observed decreases in SO₄ and OA difference and closed concentrations as T_{vap} is decreased. In contrast, the closed profile of volatile NO₃ is the result of only delayed vaporization as bounce of these particles from the vaporizer surface throughout this T_{vap} range is apparently negligible. It is interesting that the impact of delayed vaporization is observed in the closed concentration profiles of relatively high (e.g., NO₃) and low (e.g.,

SO₄ and OA) volatility species even in the case of a complex, internally mixed aerosol (Cubison, et al. 2008).

3.4 Changes in Apparent Ambient OA Oxidation with T_{vap}

The bulk of inorganic ions are contributed by relatively few species in ambient aerosol. Ambient OA, in contrast, is a poorly characterized aggregate of thousands of individual compounds. Complex OA spectra from the AMS have been deconvolved through the use of positive matrix factorization (PMF) (Paatero 1997, Ulbrich, et al. 2009) to reveal a number of OA components, many of which are consistent across diverse locations (Jimenez, et al. 2009, Ng, et al. 2010). In SOAR-2005 and other locations (Docherty, et al. 2011, Huffman, et al. 2009), the degree of oxidation and relative volatility of identified OA components vary inversely. As VTC sampling appears to provide information on the relative volatility of NR-PM₁ species, one would expect that the detected OA should become less oxidized at lower T_{vap} due to the lower volatility of the more highly oxidized OA.

Profiles for various OA oxidation metrics are shown in Figure 5. Contrary to expectations the metrics of OA oxidation such as O:C (Aiken, et al. 2008) and f_{44} actually increase as T_{vap} is decreased. This is confirmed by profiles of CO₂⁺ (which dominates m/z 44) and OA in Fig. 5b. Given that the thermal denuder data were conclusive about the lower volatility of oxidized OA in this study, the VTC results indicate that factors other than volatility must be at play in the OA composition detection in this mode. Similar results are observed for the BEARPEX study (Figure S6).

Canagaratna, et al. (2015) conclusively showed that CO₂⁺ in the AMS is formed by thermal decomposition in the vaporizer, rather than by ion fragmentation, and that the efficiency of CO₂⁺ formation from standard compounds was the same at T_{vap} =200°C as at 600°C. This, together with our VTC observations indicate that, for ambient OA, thermal decomposition increases in importance relative to molecular evaporation as T_{vap} decreases. Our data can be explained if the less volatile and more oxygenated species still undergo thermal decomposition at lower T_{vap} , while the more reduced OA species that suffer less thermal decomposition do evaporate less as observed for the inorganics. Importantly, the thermal decomposition of the oxidized species is fast so that the CO₂⁺ still appears in the difference signal, while the closed signal shows little change. Thus, the impact of thermal decomposition limits the use of the VTC sampling to infer the relative volatility of OA components, and the TD-AMS method (Huffman, et al. 2009) is preferred for this purpose.

3.5 Changes in Ambient OA MS with T_{vap}

Average absolute intensities of reduced and oxidized ions are plotted for T_{vap} = 600°C vs. 200°C in Fig. 6. Overall, the intensity of C_xH_y⁺ ions tends to decrease more than that of C_xH_yO_n⁺ ions which is consistent with OA appearing more highly oxidized at lower T_{vap} . When these spectra are investigated in detail, however, more complex sensitivities of each ion class to T_{vap} become apparent. For example, the increased scatter between C_xH_y⁺ spectra suggest a higher sensitivity of the ion class

to T_{vap} relative to $C_xH_yO_n^+$. These changes are explored further in Figure S7, which shows raw HR-AMS MS averaged throughout SOAR-2005 VTC sampling at several nominal masses having contributions from each ion class. As these plots show, $C_xH_y^+$ ions are indeed more sensitive to T_{vap} . Additionally, however, the overall sensitivity is m/z -dependent with the largest decreases occurring at small m/z and diminishing at higher m/z . This suggests that the thermal decomposition and thermally-enhanced fragmentation of chemically-reduced species is diminished substantially at lower T_{vap} .

Some individual ions have a larger absolute intensity at $T_{vap}=200^\circ\text{C}$ indicating a possible analytical improvement for some types of OA due to reduced decomposition/fragmentation at lower T_{vap} . E.g., a significant increase in the intensity of $C_{14}H_{28}^+$ (inset in Fig. 6a) is observed at $T_{vap}=200^\circ\text{C}$. The relatively small number of ions having a larger average signal at $T_{vap}=200^\circ\text{C}$ may be due to a stronger influence (for the majority of ions) of a decreased evaporation rate compared with any influence from any reduction in neutral decomposition or ion fragmentation as T_{vap} is reduced.

Difference and closed profiles of $C_xH_y^+$, $C_xH_yO_1^+$, and $C_xH_yO_{n>1}^+$, analogous to Figs. 4 and 5, are shown in Figure 7 and more clearly show differences among these ion classes. Decreases in difference concentrations proceed in the order (from largest to smallest) $C_xH_y^+ > C_xH_yO_1^+ \geq C_xH_yO_{n>1}^+$. Closed $C_xH_y^+$ and $C_xH_yO_1^+$ concentrations exhibit little, if any, decrease throughout this range of T_{vap} while decreases in closed $C_xH_yO_{n>1}^+$ concentrations mirror those of the difference signal. $C_xH_y^+$ and $C_xH_yO^+$ closed profiles have an evaporation spike at increasing temperature transitions, which is absent for $C_xH_yO_{n>1}^+$.

3.6 Apparent VTC volatilities of Major NR-PM₁ Components

VTC profiles (i.e., the fraction of mass detected at each T_{vap} relative to 600°C) for major SOAR-2005 NR-PM₁ components are shown in Figure 8a from both MS and PToF data while relative volatility profiles for each component as measured by TD (Huffman, et al. 2009) are shown in Fig. 8b for reference. Although VTC and TD profiles will differ due to the different operating principles of each measurement, each technique broadly characterizes the relative volatility of most components similarly. It is important to note that, in general, the slope of VTC profiles will steepen as component volatility decreases while the opposite is true of TD profiles.

VTC profiles for NO_3 are relatively flat indicating its relative insensitivity to T_{vap} and a relatively high volatility which is consistent with its TD profile steeply decreasing as TD temperature increases above ambient. In terms of TD measurements, the volatility of SO_4 appears to be lower than that of OA throughout the lower half of the TD temperature range. At high TD temperatures, however, NR-PM₁ composition is dominated by OA (Huffman, et al. 2009) indicating that a small fraction of OA has a volatility lower than that of SO_4 . The slopes of the VTC OA profile are consistently steeper than those of SO_4 throughout the T_{vap} range which would suggest that a majority of OA mass has a lower volatility than SO_4 in contrast to TD results. The apparent volatility of NH_4 is one source of contrast

between the two techniques. Like those of NO_3 , the VTC profiles for NH_4 are relatively flat and NH_4 appears to be insensitive to T_{vap} . These profiles would be reasonable if the overwhelming majority of NH_4 was contributed by NH_4NO_3 . As a TD profile intermediate to that of NO_3 and SO_4 indicates, however, additional contributions from $(\text{NH}_4)_2\text{SO}_4$ should lower NH_4 volatility relative to NO_3 . This discrepancy may be due to relatively large errors associated with VTC data obscuring small differences among the different component VTC profiles.

4. Conclusions

A T_{vap} control module was successfully operated on multiple AMS instruments during the course of the SOAR-2005 and BEARPEX-2007 field campaigns without negative impacts on either the quantitative capacity or the physical integrity of the instrument. Overall, the sensitivity of major NR- PM_{10} components to T_{vap} is consistent with their relative volatility: higher volatility species (e.g. NO_3) show little change as T_{vap} is decreased while lower volatility species (OA and SO_4) display a clear decrease in signal. Changes in the apparent size distributions are consistent with those results. Some reduced OA ions at higher m/z exhibit a substantially lower tendency to undergo thermal decomposition or thermally-enhanced fragmentation, in some cases with enhanced signal at lower T_{vap} , indicating that this method may improve the analysis of some aerosol systems dominated by reduced (C_xH_y^+) ions. The overall OA MS, however, changes substantially with changes in T_{vap} and the observed trends cannot be simply interpreted to derive volatility information as a result. However, a relative increase in O:C and CO_2^+ as T_{vap} decreases is likely due to continuing thermal decomposition of oxidized species combined with lower evaporation of reduced species. Thus it appears that the reactive tungsten vaporizer surface and the inability of the standard AMS vaporizer to reach $T_{\text{vap}} < 200^\circ\text{C}$ (that can be achieved with other aerosol thermal desorption methods) limit the ability of this method to study the volatility of oxidized organic species. Future work should explore the detection of different inorganic species (e.g. different sulfate, nitrate, or chloride salts), of inorganic vs. organic nitrates and sulfates, and of different types of reduced organic species, as the VTC system may provide a more direct characterization of volatility as well as aid chemical identification in such systems. A custom vaporizer that could present a more chemically-inert surface and operate at lower temperatures may also expand the information extractable with this technique.

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Figures

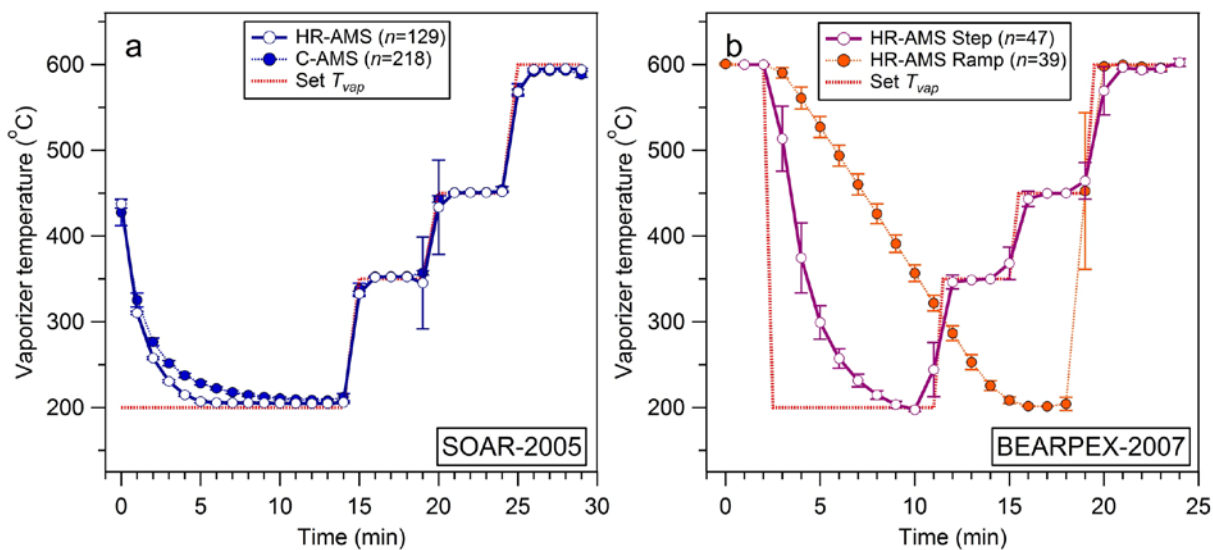


Figure 1. Average profiles of both set and actual AMS T_{vap} from VTC operation during (a) SOAR-2005 and (b) BEARPEX-2007. Error bars in each case represent twice the standard deviation for each T_{vap} step throughout the duration of VTC sampling.

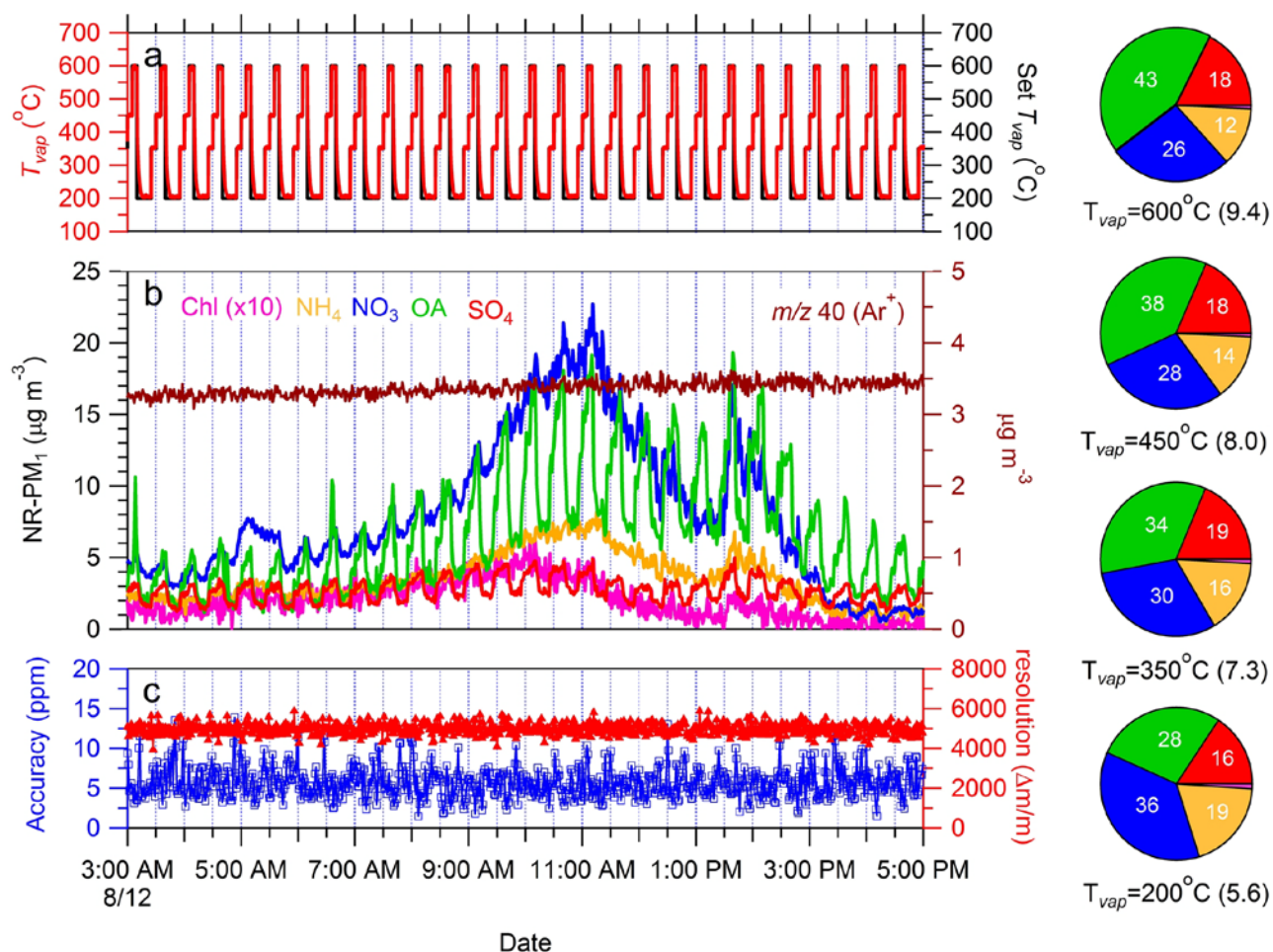


Figure 2. Time series of (a) set and actual T_{vap} , (b) major NR-PM₁ species and m/z 40 (Ar^+) concentrations, and (c) quality of fit parameters for high resolution peak fitting from a short interval of VTC sampling on the HR-AMS during SOAR-2005. Average NR-PM₁ composition at each T_{vap} are shown by the pie charts to the right and average NR-PM₁ concentrations are shown in parentheses. At each T_{vap} , the relative contribution of Chl was $\leq 2\%$.

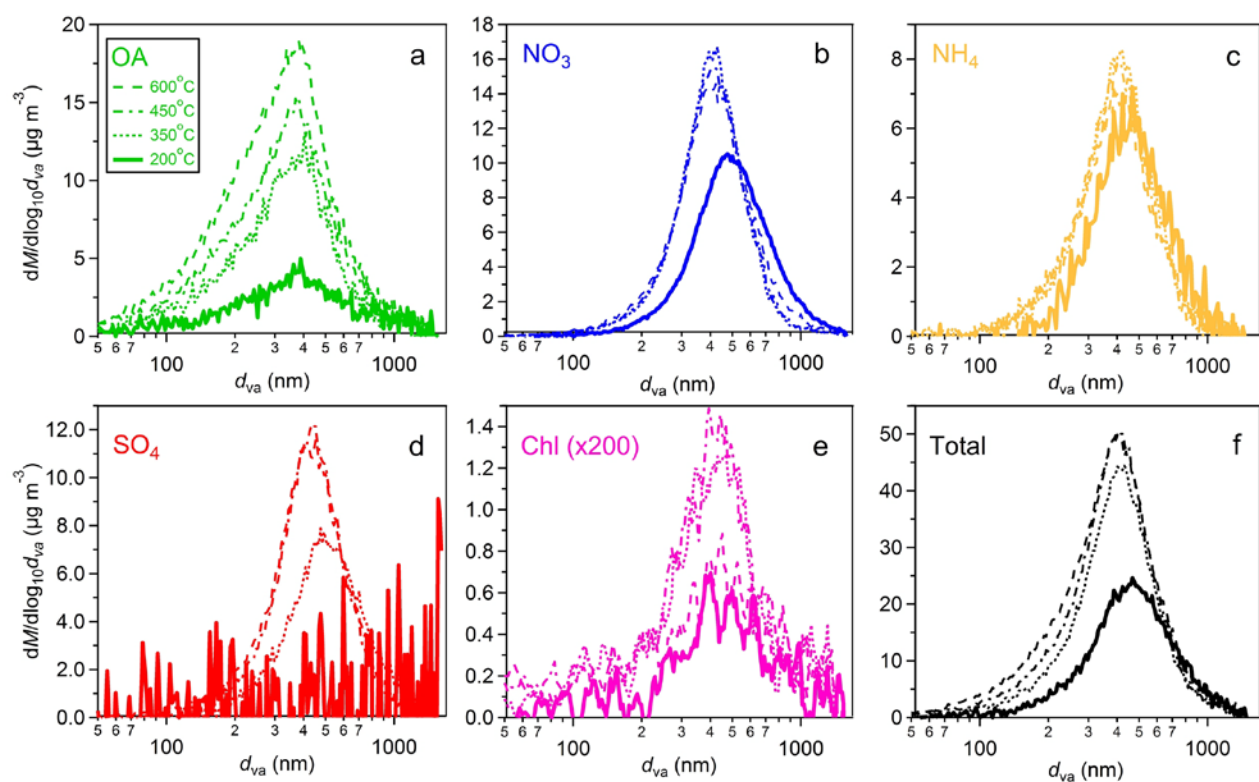


Figure 3. C-AMS apparent size distributions of NR-PM₁ (a) OA, (b) NO₃, (c) NH₄, (d) SO₄, (e) Chl, and (f) total at each different T_{vap} from SOAR-2005.

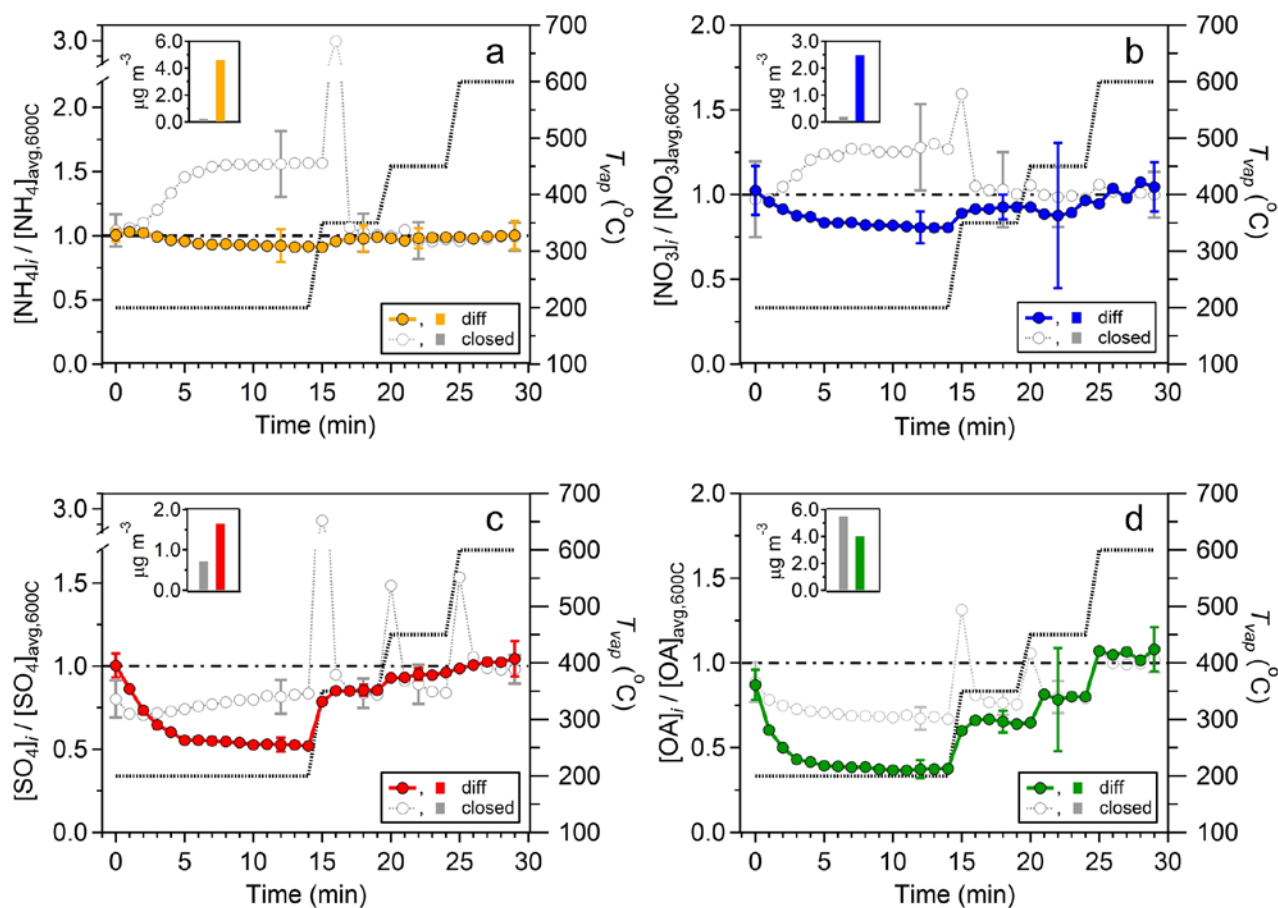


Figure 4. Average difference and closed profiles of (a) NH_4 , (b) NO_3 , (c) SO_4 , and (d) OA during HR-AMS SOAR-2005 VTC sampling. Individual data points represent average concentrations normalized to $T_{\text{vap}} = 600^\circ\text{C}$ concentrations for each cycle throughout VTC sampling while error bars represent twice the standard deviation. NH_4 profiles were generated using high resolution data. Average absolute difference and closed concentrations at $T_{\text{vap}} = 600^\circ\text{C}$ are shown by bar plots inset into each panel. We note that the total signals include general instrument background that is not related to sampled aerosols, unlike the method of Huffman et al. (2009) that attempted to subtract that component by fitting the fraction of the background that does not respond to ambient aerosol variations.

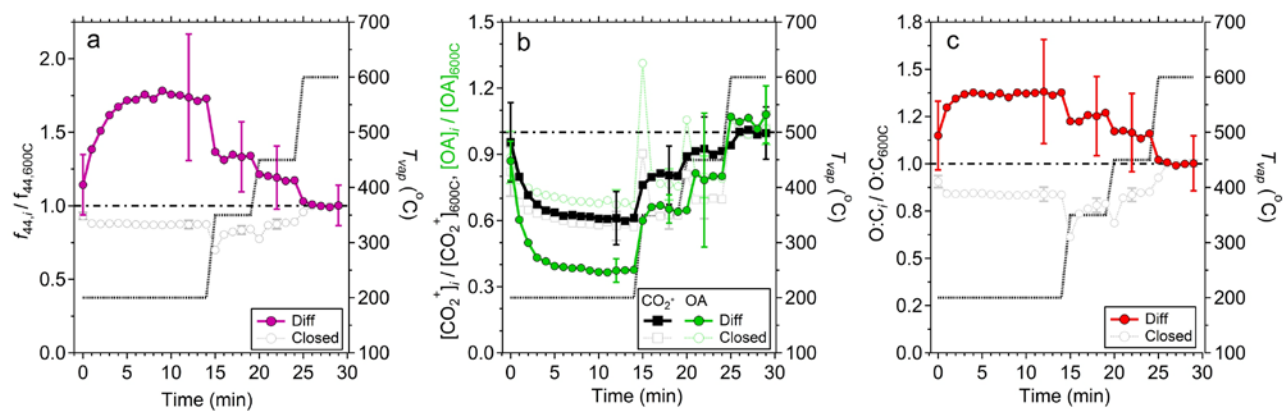


Figure 5. Average HR-AMS difference and closed profiles of (a) f_{44} , (b) CO_2^+ and NR-PM₁ OA, and (c) O:C ratio. Error bars in each case represent twice the standard deviation for each respective measurement throughout the duration of VTC sampling. Note that a limited number of error bars are shown at each set T_{vap} (e.g., 200, 350, 450, and 600°C) for clarity.

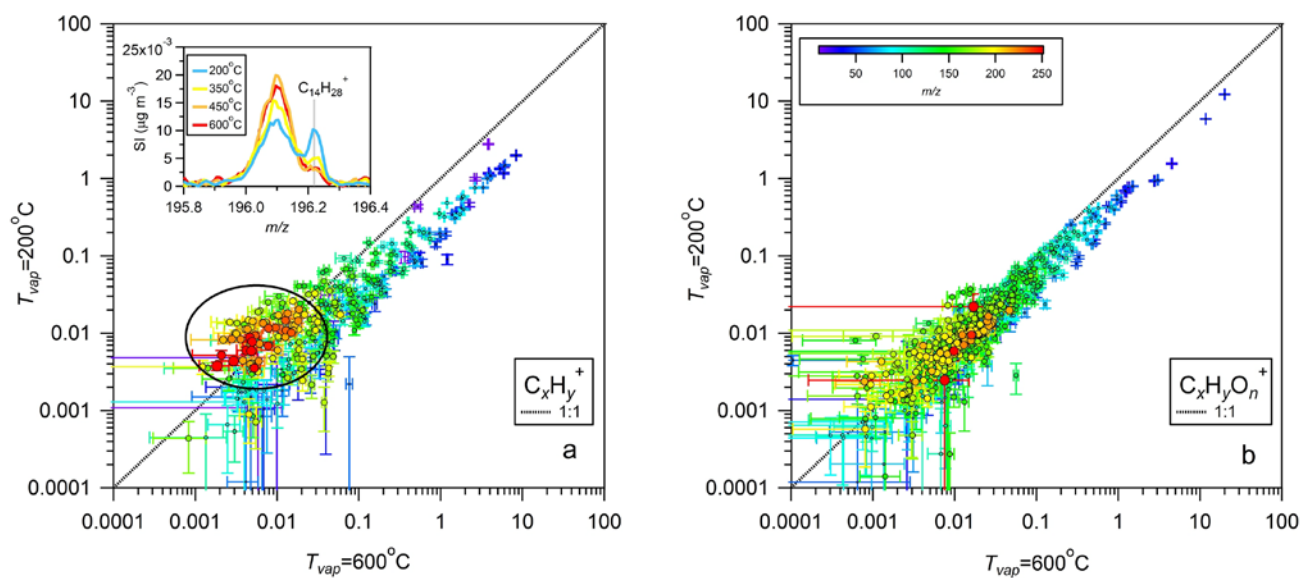


Figure 6. Average SOAR-2005 HR-AMS (a) $C_xH_y^+$ and (b) $C_xH_yO_n^+$ mass spectra at $T_{vap}=200^\circ\text{C}$ versus $T_{vap}=600^\circ\text{C}$. Error bars for each data point represent the estimated ion counting error for each ion at each different T_{vap} .

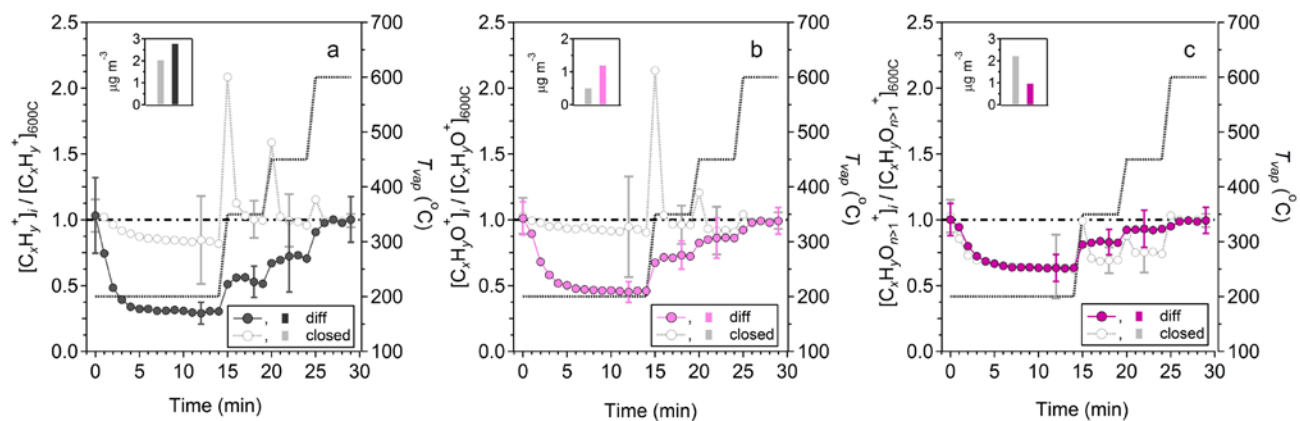


Figure 7. Average HR-AMS difference and closed profiles of (a) $C_xH_y^+$, (b) $C_xH_yO^+$, and (c) $C_xH_yO_{n>1}^+$ ion classes. Average absolute difference and closed concentrations at $T_{vap}=600^\circ C$ are shown by bar plots inset into each panel.

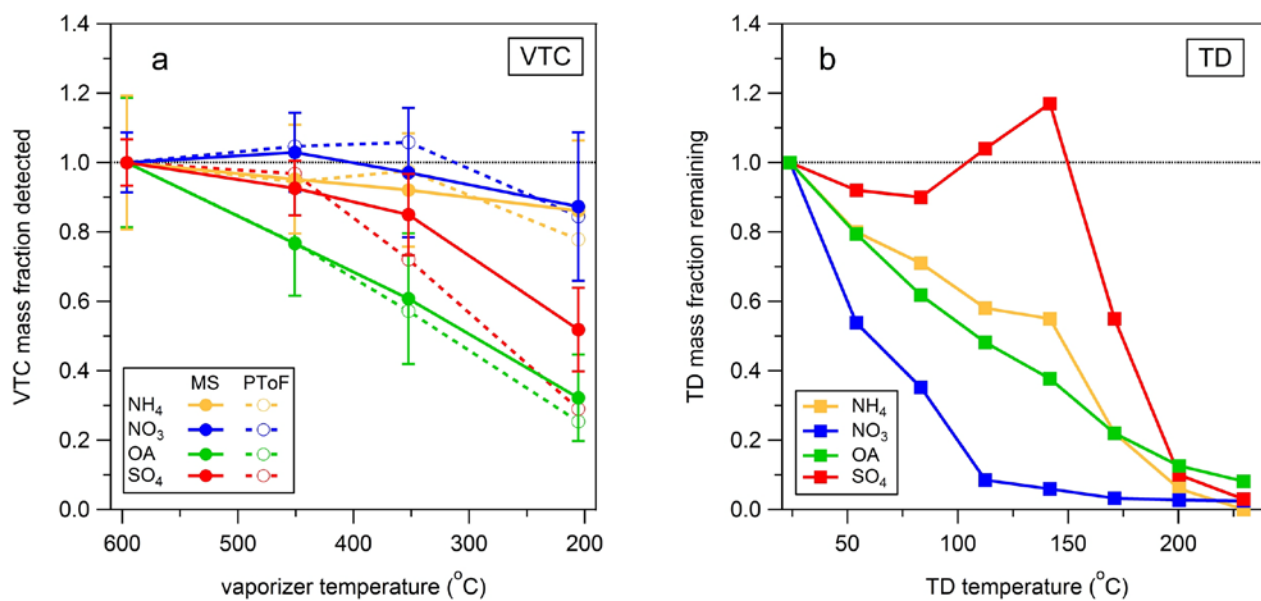


Figure 8. SOAR-2005 VTC (a) and TD-AMS (b) profiles of major NR-PM₁ components.

Supplemental Information

Effect of Vaporizer Temperature on Ambient Non-Refractory Submicron Aerosol Composition and
Mass Spectra Measured by the Aerosol Mass Spectrometer

Kenneth S. Docherty, Michael Lewandowski, and Jose L. Jimenez

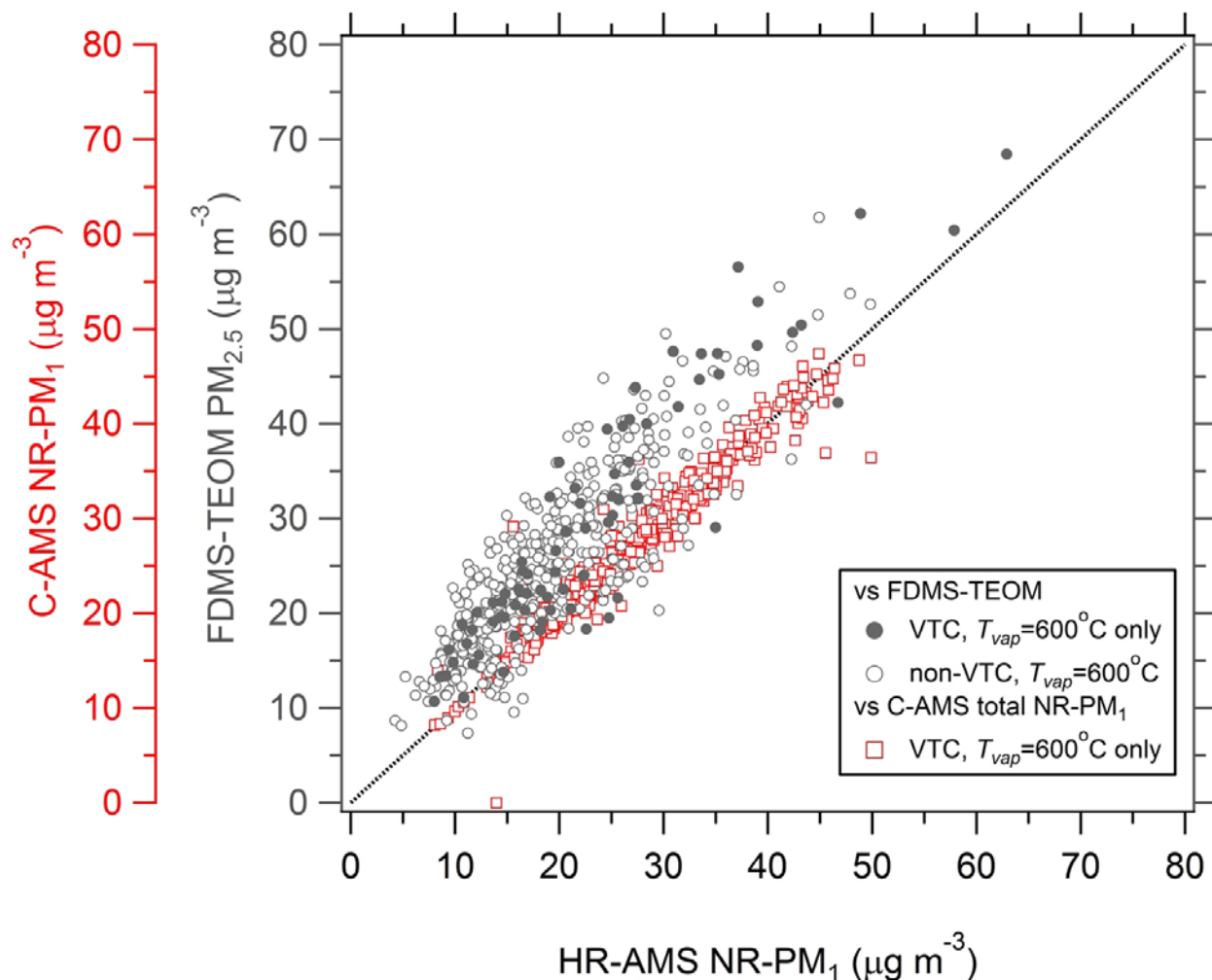


Figure S1. Comparison of SOAR-2005 HR-AMS NR-PM₁ measurements with corresponding collocated FDMS-TEOM and C-AMS measurements. Hourly measurements obtained during VTC operation when $T_{vap}=600^{\circ}\text{C}$ (VTC) and standard sampling periods (non-VTC, constant $T_{vap}=600^{\circ}\text{C}$) display the same relationship when compared with FDMS-TEOM measurements (see Docherty et al., 2011 for details regarding this comparison). Measurements obtained during VTC operation when $T_{vap}=600^{\circ}\text{C}$ are also highly correlated ($r^2=0.94$) with C-AMS (constant $T_{vap}=600^{\circ}\text{C}$) total NR-PM₁ obtained over the same period.

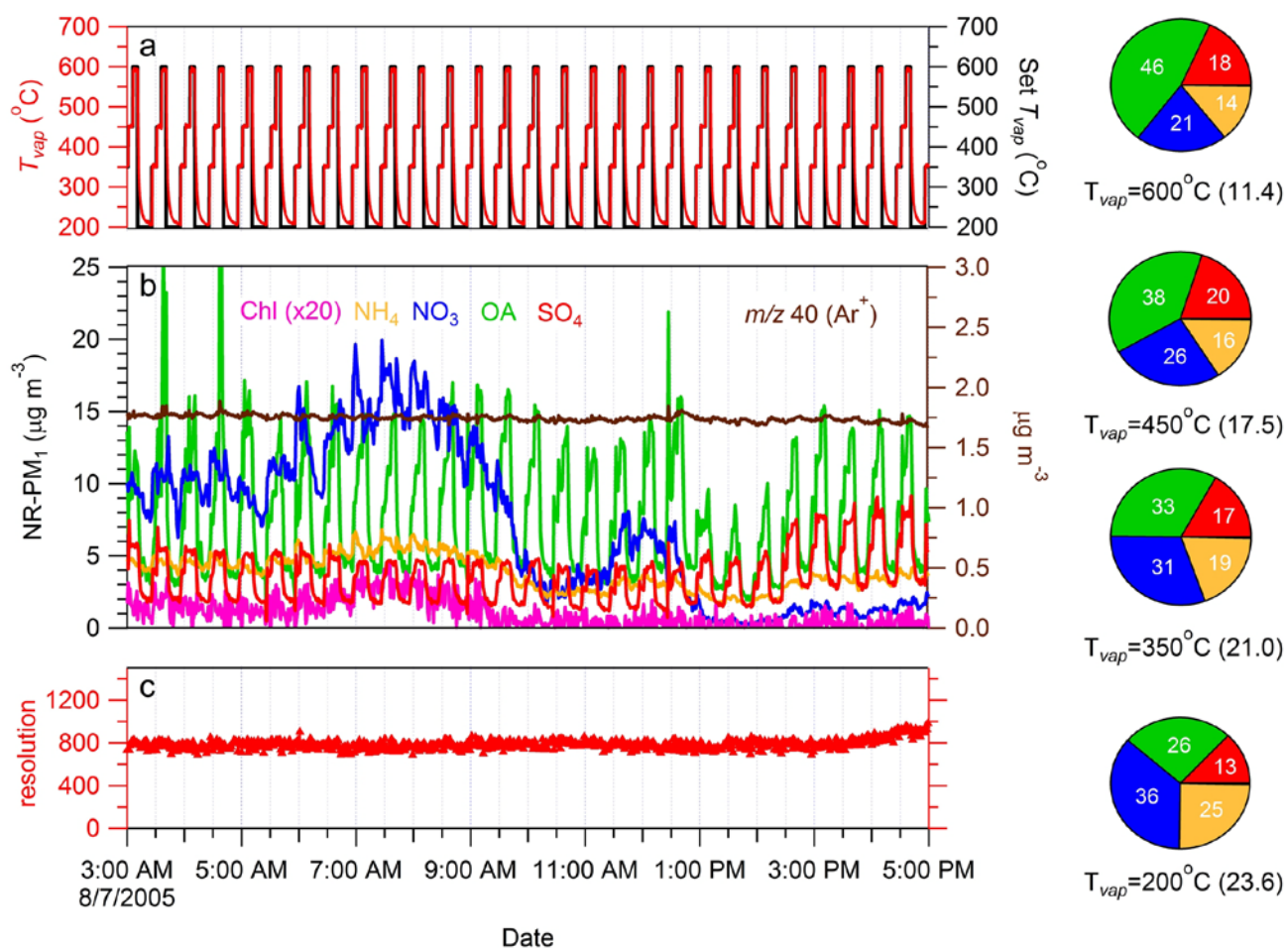


Figure S2. Time series (a) setpoint and actual T_{vap} , (b) major NR-PM₁ species and m/z 40 (Ar^+) concentrations, and (c) quality of fit parameters for high resolution peak fitting from a small window of VTC sampling on the C-AMS during SOAR-2005.

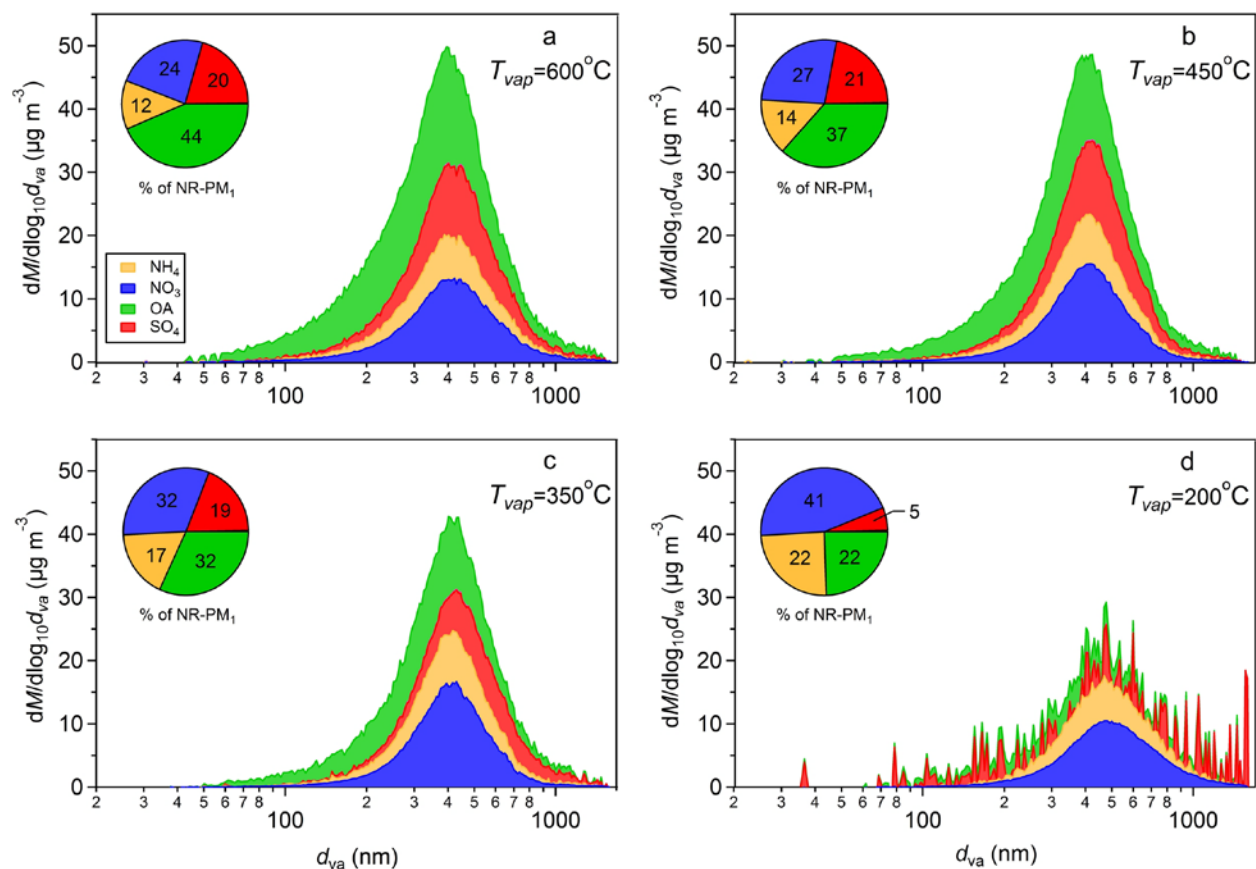


Figure S3. C-AMS NR-PM₁ component apparent size distributions at T_{vap} = (a) 600°C, (b) 450°C, (c) 350°C, and (d) 200°C averaged over the periods of VTC sampling during SOAR-2005. Pie charts are included to show the apparent composition obtained from PToF mode at each T_{vap} . Chl is not shown due to its small contribution to NR-PM₁ (see Fig. 6 in the main text for the relative evolution of the Chl size distributions).

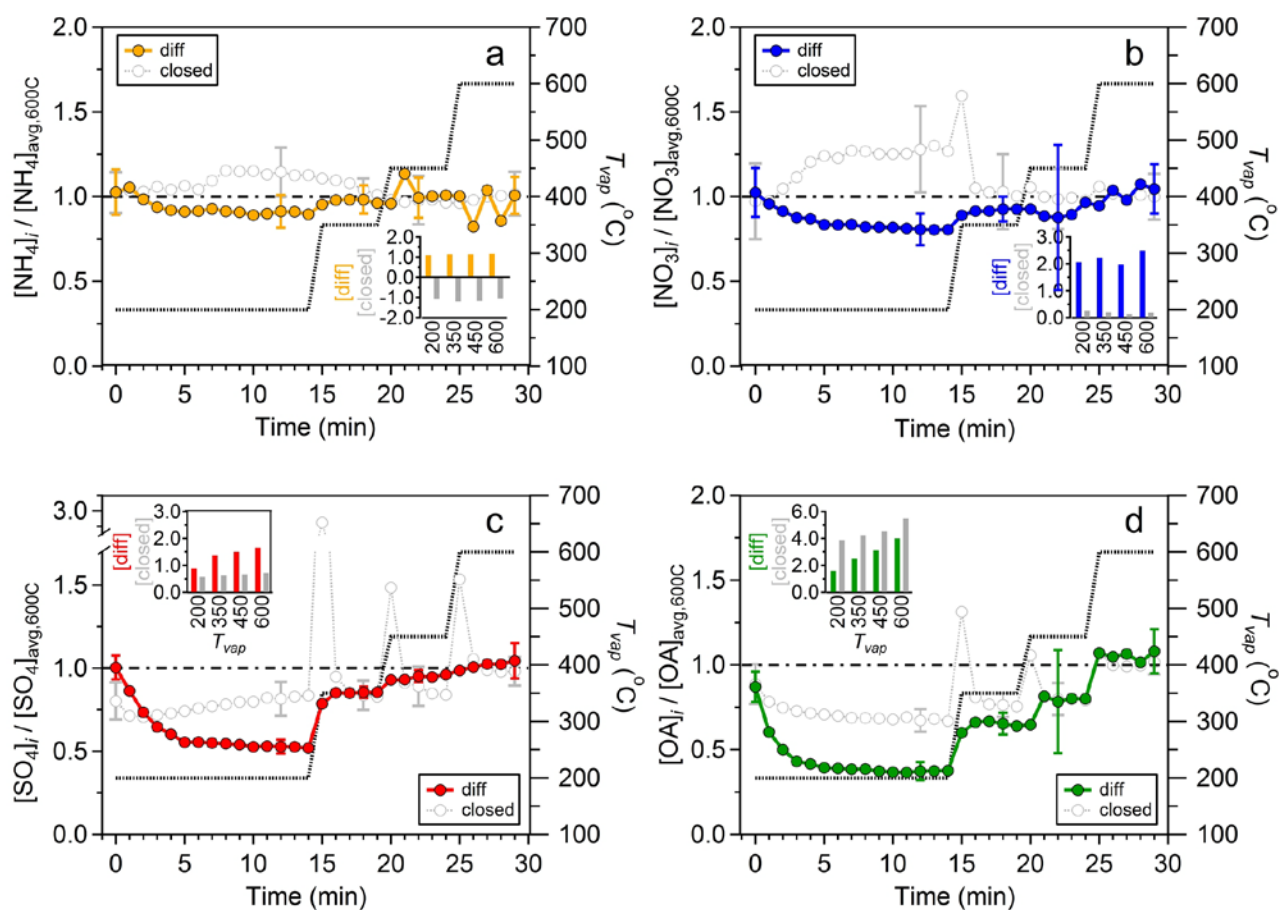


Figure S4. Average C-AMS difference and closed concentrations of (a) NH_4 , (b) NO_3 , (c) SO_4 , and (d) OA during SOAR-2005. Individual data points represent average concentration at each minute throughout VTC of the T_{vap} cycle while error bars represent the standard error of each average.

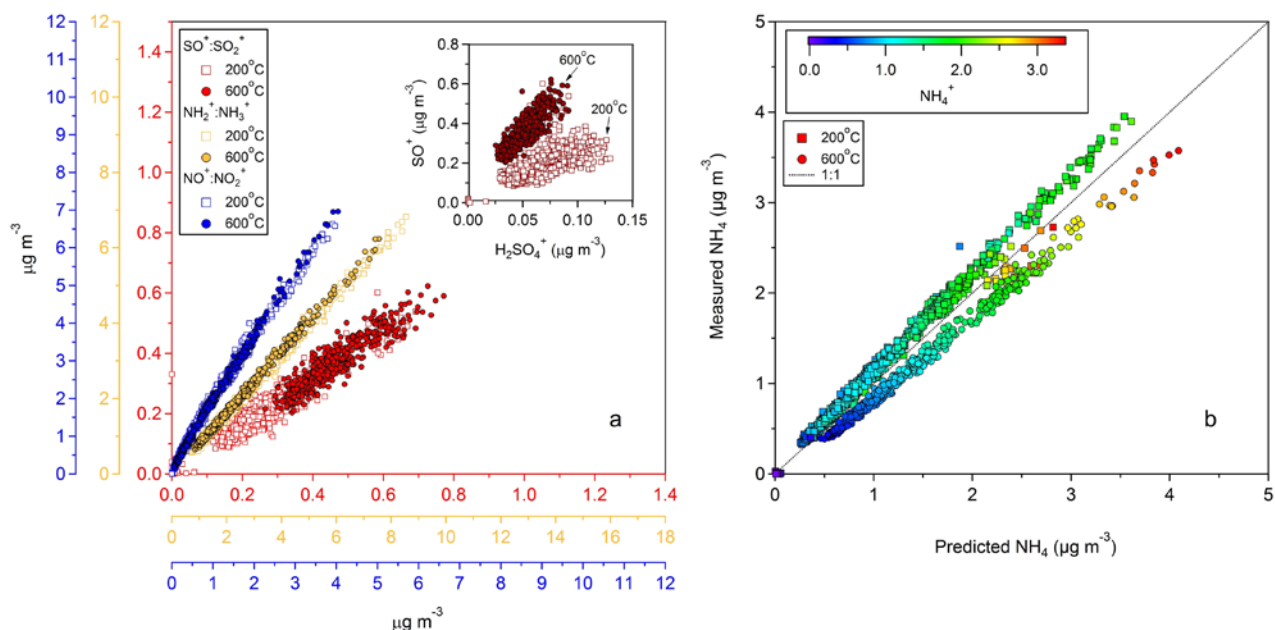


Figure S5. a) Comparison of major high-resolution ions from NR-PM₁ NH₄ (NH₂⁺:NH₃⁺), NO₃ (NO⁺:NO₂⁺), and SO₄ (SO⁺:SO₂⁺) at T_{vap}=600°C and 200°C. The ratio of these ions is largely unchanged between these two temperatures. The ratio between a second set of SO₄ ions (SO⁺:H₂SO₄⁺, inset) does change slightly at the vaporizer temperature extremes, however, based on the minor contribution of the H₂SO₄⁺ ion to the overall SO₄ spectrum the different ratios are largely inconsequential. b) Measured versus predicted NH₄ concentrations at 200°C and 600°C. The change in the NH₄ balance between the two T_{vap} extremes is due to a decrease in SO₄ concentrations at T_{vap}=200°C while NO₃, Chl, and NH₄ concentrations are largely unchanged.

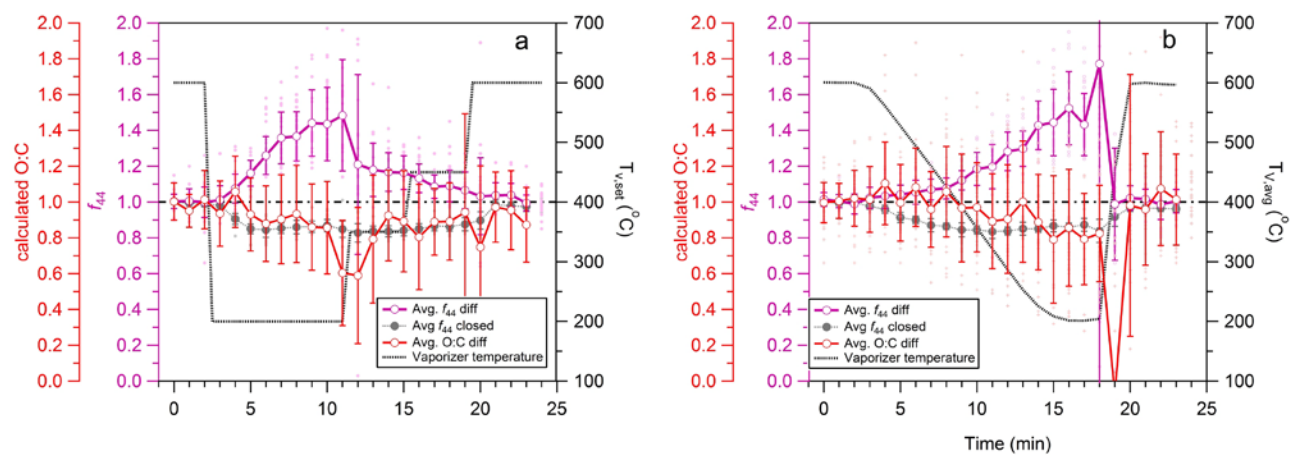


Figure S6. Average indicators of OA oxidation (f_{44} and OA) throughout VTC (a) stepped T_{vap} and (b) decreasing linear ramp of T_{vap} during BEARPEX-2007.

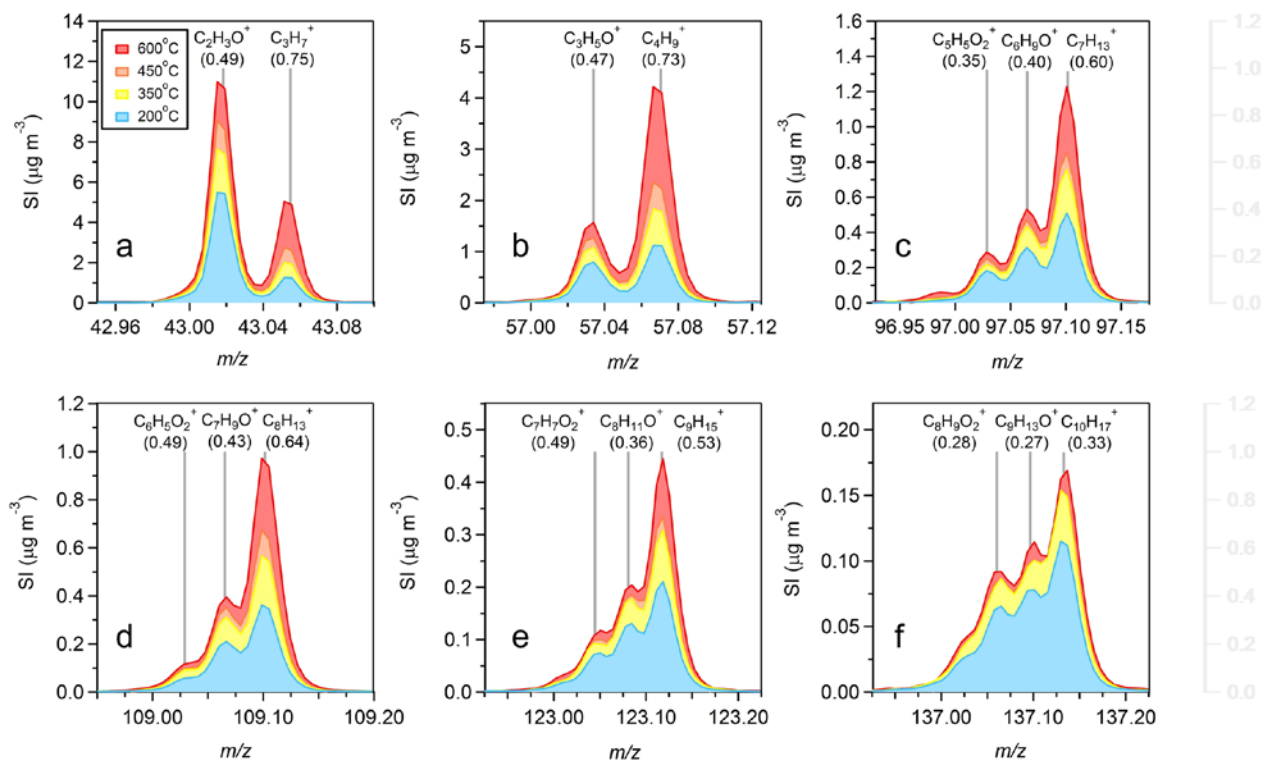


Figure S7. Raw high resolution mass spectra over a wide m/z range showing different T_{vap} -dependent sensitivities of reduced and oxidized ions. As T_{vap} decreases, the absolute intensity of reduced (C_xH_y^+) ions decreases more than that of oxidized ($\text{C}_x\text{H}_y\text{O}_1^+$ and $\text{C}_x\text{H}_y\text{O}_{n>1}^+$) ions. For example, at m/z 43, C_3H_7^+ decreases by 75% while $\text{C}_2\text{H}_3\text{O}^+$ decreases by only 49%. Similar trends can also be seen at m/z 57 between C_4H_9^+ (73% decrease) and $\text{C}_3\text{H}_5\text{O}^+$ (47% decrease). At m/z 's where more than one oxidized ion is present, the decrease in absolute intensity generally proceeds in the order $\text{C}_x\text{H}_y^+ > \text{C}_x\text{H}_y\text{O}_1^+ \geq \text{C}_x\text{H}_y\text{O}_{n>1}^+$.