Comprehensive characterization of atmospheric organic carbon at a forested site


Quality control.
The data from many of the instruments consist of 2D matrices with both large numbers of time points as well as large numbers of individual compounds. Because many of the individual ions that are measured correspond to compounds that are unidentified, some quality control of the data was required that is independent of molecular identity. A basic screen was applied to all the time series to eliminate features that are likely non-physical or associated with instrument background or electronic interference (e.g. signal spikes). Approximately 1% of the time points were excluded.

Classes of organic species not measured by this instrument suite.
The instrumentation suite measures most known classes of atmospheric organic species, including oligomeric species in the aerosol phase, which are detected by both the AMS and the MOVI-CIMS. The main organic classes which are not measured by any of the five instruments...
are volatile reduced species, namely $C_{\leq 13}$ alkanes and $C_{\leq 4}$ alkenes, and gas-phase ELVOCs, which condense on particles rapidly after formation and so are present in only very small concentrations. It is also possible that some functionalized (non-acidic) IVOCs may not be detected efficiently by the instrument suite; such compounds can in principle be detectable by the PTR-MS and TD-EIMS, but may be lost to inlet surfaces (PTR-MS) or undergo thermal decomposition (TD-EIMS) prior to mass spectrometric detection.

**Rate coefficients used in reaction rate calculations.**

The literature rate coefficients used in this study are presented in Table S1. All values were obtained from the Master Chemical Mechanism (v3.3)\(^3\)\(^-\)\(^4\) (http://mcm.leeds.ac.uk/MCM), which in turn were generally obtained from IUPAC recommendations\(^5\). All the rates were calculated for a temperature of 20 °C for simplicity. This value is marginally higher than the measured mean temperature (17.5 °C), leading to only a small difference in the calculated rates. Photolysis rates were calculated as a function of diurnal hour for solar zenith angles from the midpoint of the campaign and subsequently averaged.

**Table S1.** Rate coefficients used in this study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>O$_3$ Rate Coefficient (cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>OH Rate Coefficient (cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>NO$_3$ Rate Coefficient (cm$^3$ molec$^{-1}$ s$^{-1}$)</th>
<th>Photolysis rate (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>-</td>
<td>8.50E-12</td>
<td>-</td>
<td>2.83E-05</td>
</tr>
<tr>
<td>Methanol</td>
<td>-</td>
<td>9.00E-13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>-</td>
<td>1.50E-11</td>
<td>-</td>
<td>1.35E-06</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>-</td>
<td>4.50E-13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol</td>
<td>-</td>
<td>3.20E-12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acetone</td>
<td>-</td>
<td>1.05E-13</td>
<td>-</td>
<td>5.9E-06</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>-</td>
<td>8.00E-13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isoprene</td>
<td>1.27E-17</td>
<td>1.00E-10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>1.22E-18</td>
<td>2.90E-11</td>
<td>-</td>
<td>6.31E-06</td>
</tr>
<tr>
<td>Compound</td>
<td>Rate Coefficient</td>
<td>Rate Coefficient</td>
<td>Rate Coefficient</td>
<td>Rate Coefficient</td>
</tr>
<tr>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Methylglyoxal</td>
<td>1.30E-11</td>
<td>-</td>
<td>5.35E-05</td>
<td></td>
</tr>
<tr>
<td>MEK</td>
<td>1.10E-12</td>
<td>-</td>
<td>1.77E-05</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.20E-12</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>MBO</td>
<td>1.00E-17</td>
<td>1.60E-10</td>
<td>1.10E-14</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>-</td>
<td>5.70E-12</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td>-</td>
<td>2.31E-11</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>8.70E-17</td>
<td>5.25E-11</td>
<td>6.10E-12</td>
<td></td>
</tr>
<tr>
<td>Sesquiterpenes (avg)(^a)</td>
<td>1.16E-14</td>
<td>1.6E-10</td>
<td>1.8E-11</td>
<td></td>
</tr>
<tr>
<td>Humulene</td>
<td>1.16E-14</td>
<td>2.93E-10</td>
<td>3.9E-11</td>
<td></td>
</tr>
<tr>
<td>Longifolene</td>
<td>0</td>
<td>4.7E-11</td>
<td>6.8E-13</td>
<td></td>
</tr>
<tr>
<td>Aromadendrene</td>
<td>6.5E-15</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Alloaromadendrene</td>
<td>6.5E-15</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Muurolene</td>
<td>9.7E-15</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The average rate coefficients for sesquiterpenes were calculated from TAG speciated sesquiterpene concentrations and associated rate coefficients. The ozone rate coefficient for aromadendrene was obtained from Pollman et al\(^b\), and the coefficients for aromadendrene and muurolene were estimated to be 1x and 1.5x the rate of aromadendrene. These speciated sesquiterpenes make up about 10% of the total sesquiterpene signal from the PTR-MS. Photolysis rates are calculated and averaged for solar zenith angles corresponding to the middle of the campaign.

**Uniformity of concentrations over the entire campaign.**

The values reported in this work reflect campaign averages for instruments, each of which had somewhat different measurement periods. Combining them into a single campaign average is reasonable given the relatively uniform time series, in which approximately the same concentrations and diurnal patterns were measured day to day for all instruments. Figure S1 shows the full time series for two major organic types, monoterpenes (panel a, from PTR-MS measurement) and OA (panel b, from AMS measurements), plotted diurnally such that the overall variability is apparent. Monoterpenes are highly reactive and have highly variable emissions, and therefore should give an upper limit to the amount of variability within the
dataset. OA is much longer lived, and should give a lower limit to the variability due to day to
day differences in chemistry. Both quantities have approximately a factor of two spread in their
concentrations, with the exception of a few much higher points for monoterpenes (which do not
significantly impact the overall average); further, no obvious campaign-wide trends are seen in
either dataset. This indicates that there were no significant departures from campaign-averaged
chemistry during the campaign, supporting the use of overall diurnal averages, and allowing for
comparisons of measurements taken over somewhat different periods. The concentrations and
calculated fluxes also vary over the course of the day, but these differences do not significantly
change the overall conclusions, and a 24-hour average is therefore used throughout the text
(except for in the discussion of diurnal cycles, below). The uniformity of the time series gives

**Figure S1.** Variability of measured species during BEACHON-RoMBAS, illustrated by the
campaign time series of summed monoterpenes (panel a) and organic aerosol (panel b). The dashed
line is the average, the whiskers extend to the 5th and 95th percentile, and the box contains the median
bounded by the 25th and 75th percentiles. The variability is approximately a factor of two for both
monoterpenes (short-lived) and organic aerosol (long-lived) with no significant departures from the
average diurnal profile excepting a handful of points. This suggests that the chemistry was similar
day-to-day, and supports the comparison of average data from instruments in this study that had
somewhat different sampling periods.
confidence in the comparability of the data sets from the five instruments in this study in spite of
the differences in their collection periods.

**Estimates of vertical mixing time.**

Approximate estimates of the mixing time can be constructed from the roughness
velocity (u*) and Monin-Obukhov length (L, a measure of atmospheric stability) available for
the field site, which enable the calculation of the vertical eddy diffusion coefficient (K_{zz})^7; the
mixing timescale is calculated by dividing K_{zz} by the square of the boundary layer height. The
diurnally-averaged timescale ranges from 8 minutes during midday (when convection is strong)
to a maximum of 6.3 hours at night (when the boundary layer is stable). Because K_{zz} is expected
to change with changing height, this estimate constructed from the surface-layer sonic
measurements may not accurately describe the overall mixing time. However, the mixing time
during the day can also be estimated using the convective velocity w* (approximately 1 m/s^7),
resulting in a time of about 18 minutes. This is reasonably comparable to the value calculated
using the M-O methods, and suggests these estimates of mixing times are reasonable.

**Diurnal trends.**

Diurnal trends for the campaign are shown in Figure S2 and S3. Such trends can result
from a number of factors, including changes to emissions (which in turn depend on temperature,
and, in some cases, light), oxidant levels, transport, vertical mixing, and boundary layer height.
Figure S2a shows average diurnal profiles in temperature and photosynthetically active radiation
(PAR) for the campaign (1 July to 27 Aug); both increase at the same time starting around 6 h,
Figure S2: Campaign-average diurnal trends. Panel a: temperature and PAR; b: boundary layer height; c: concentrations of organic carbon for each organic class; d: carbon-weighted $n_C$ for each class; e: carbon-weighted $\text{OS}_C$ for each class; f: average $n_C$ and $\text{OS}_C$ for all measured organic carbon.
with temperature reaching a maximum of 26°C (from a low of 9°C) around 13 h. Light intensity reaches a maximum slightly earlier, and decreases much more rapidly than does temperature. This leads to emissions of temperature- and light-dependent compounds increasing sharply together in the morning, and temperature-driven emissions (e.g., some monoterpenes) persisting longer than compounds with strong light-dependent emissions (e.g., MBO) in the afternoon. The resulting concentrations are also a strong function of the boundary layer height.

**Figure S3**: Average 2DVBS distributions of ambient organic species measured during the daytime (panel a, 06:00 to 17:00) and nighttime (panel b, 18:00 to 05:00). Day-night differences are consistent with the diurnal plots in Fig. S2. Differences include substantially higher levels of MBO (due to higher emissions), higher levels of formic and acetic acids (due to higher emissions and/or photochemical formation), and lower levels of monoterpenes (due to the higher boundary layer) during the daytime. Additionally monoterpenes and S/IVOC levels are higher during the nighttime, possibly due to the low boundary layer and the lack of photochemical sinks.
(S2b) and the intensity of photochemistry, both of which peak in midday; this can lead to lower concentrations even though emission rate of primary compounds and formation rates of secondary compounds are highest at this time.

Figures S2c-f and S3 show diurnal changes to the amounts and properties of the measured organic carbon. Figure S2c shows diurnal changes to each of the categories of organics; diurnal trends in carbon number \((n_c)\) and oxidation state \((\overline{O}_S)_c\) for each category are given in Figs. S2d and S2e, respectively, and the average \(n_c\) and \(\overline{O}_S_c\) for all measured organic species are given in Figure S2f. VOC concentrations increase sharply in the morning with the onset of light-driven emissions (e.g. MBO) and to a smaller degree with increasing temperature-driven emissions (monoterpenes) into a shallow boundary layer. Concentrations decrease sharply in the late morning due to photooxidation and the boundary layer height increasing to an afternoon peak of about 1100 m. Concentrations rise again in the evening as photochemistry slows and temperature-driven emissions (e.g. monoterpenes) continue into a shrinking boundary layer (which eventually reaches a midnight minimum of about 100 m). This diurnal pattern of MBO and monoterpene emissions is reflected in Figure S3, as well as in the average carbon number for VOCs (Fig. S2d). Secondary, reactive species (OVOCs and S/IVOCs) behave similarly, but with somewhat delayed profiles due to their formation from oxidation processes. The long-lived VOCs show substantial variability over the course of the day, indicating their sources (emissions, secondary formation, influx) and sinks (efflux) are important over these timescales, even though oxidative loss is not. This lack of oxidation explains why their concentrations remain high throughout the afternoon, with no characteristic dip. Diurnal changes in LL-VOCs are driven by increases in acetone and formic acid (by emissions and/or secondary production) during the daytime; these increases lead to the large increase in \(\overline{O}_S_c\) (but no change
to $n_c$) over the daylight hours. OA stays relatively constant over the course of the day, with a
distinct increase in $\overline{OS}_C$ during the daytime (which is also reflected in the $\overline{OS}_C$ of S/IVOCs),
possibly indicating more intense oxidation (aerosol aging or formation of more-oxidized SOA)
during this time.

Lower-limit calculations of organic carbon distributions.
The distributions of organic carbon provided in the text (Figs 1c-e, 2, and 3) all assume no
overlap between the carbon measured by different instruments (except in unambiguous cases of
overlap), providing an upper limit for the amount of carbon measured. The specific areas of
overlap that are accounted for in the upper limit case are: AMS and CIMS particle phase (for
which the AMS measurement is used), formic acid in the PTR-MS and CIMS (for which CIMS
measurement is used), and sesquiterpenes in the TAG and PTR-MS (for which the PTR-MS
measurement is used). The corresponding lower limits in carbon concentrations, in which
maximal overlap is assumed, are shown in Figure S4. Results are not dramatically different than
those from the upper-limit calculation: the total loading is reduced by $4.1 \mu g/m^3 (15\%)$, with the
largest differences being the loadings of S/IVOCs (since they are measured by the most
instruments). In almost all cases these such upper-limit/lower-limit differences (including in
individual “bins” in Figs. 1 and S4) are smaller than measurement uncertainty (error bars). Thus
the two cases agree to within error of the measurements, and details of the treatment of
instrument overlap does not substantially affect conclusions about the overall amounts,
properties, or reactivity of the measured organic species.
Scaling of OH reactivity by emissions.

OH reactivity was not measured in 2011, but were measured the previous year as part of the BEACHON-ROCS campaign. In order to extrapolate the 2010 OH reactivity to 2011, the differences in estimated emissions of the species primarily responsible for OH reactivity were used. These differences in emissions are themselves calculated from differences in the known temperature and PAR and the equations given in Kaser et al. for temperature- and light-dependent emissions of BVOCs. MBO and monoterpenes are the two largest sources of OH reactivity (59% of the total), and are the only significant sources of OH reactivity for which emissions measurements are available. Therefore, the year-to-year difference in emissions for these species only were used to calculate the scaling factor for OH reactivity. The 2011 OH reactivities for MBO and monoterpenes were normalized by their 2011 emissions, and the resulting factors used to calculate the 2010 MBO and monoterpane OH reactivities. These were...
then scaled proportionally such that their sum was equal to the 2010 measured value for total OH reactivity (10 s\(^{-1}\)). These scaled OH reactivities were then multiplied by the 2010-11 fractional changes in emissions to estimate the 2011 total reactivity (8 s\(^{-1}\)). Although emissions of monoterpenes and other BVOCs increased from 2010 to 2011, the relative contribution of MBO to the OH reactivity is so much larger that its decrease from 2010 to 2011 dominates the overall change.

**SOA formation estimates.**

For all known/studied SOA precursors, the SOA yields, OM/OC values, and carbon yields (equal to SOA yield divided by OM/OC), along with references for each, are given in Table S2. To ensure proper comparison with the oxidation flow reactor (OFR) measurements, these include only measurements from experiments in which RO\(_2\) chemistry is dominated by reaction with \(\text{HO}_2\), with no influence from aqueous-phase uptake, etc. Relative error for carbon yields is estimated to be 30%. For unknown/unmeasured species (unspeciated (O)VOCs and all I/SVOCs except sesquiterpenes), yields are estimated from the \(c^*\) of the precursor species, using the general approach of Donahue et al.\(^{10}\) The functional form used is shown in Figure S5; error in this approach is likely high, conservatively assumed to be a factor of three (indicated by shaded grey region in Figure S5). Note that the resulting range includes the strict upper limit of a 100% carbon yield for low-volatility species.
Table S2. Aerosol yields used in this study.

<table>
<thead>
<tr>
<th>SOA precursor</th>
<th>Aerosol yield ($c_{OA} = 1.8$)</th>
<th>OM/OC</th>
<th>Aerosol carbon yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sesquiterpenes</td>
<td>13.2%\textsuperscript{a}</td>
<td>1.47\textsuperscript{d}</td>
<td>9.0%</td>
</tr>
<tr>
<td>Methacrolein</td>
<td>2.4%\textsuperscript{b}</td>
<td>1.87\textsuperscript{b}</td>
<td>1.3%</td>
</tr>
<tr>
<td>Isoprene</td>
<td>3.2%\textsuperscript{a}</td>
<td>1.91\textsuperscript{b}</td>
<td>1.7%</td>
</tr>
<tr>
<td>Toluene</td>
<td>13.8%\textsuperscript{a}</td>
<td>2.0\textsuperscript{b}</td>
<td>6.9%</td>
</tr>
<tr>
<td>Xylene</td>
<td>21.6%\textsuperscript{c}</td>
<td>2.1\textsuperscript{b}</td>
<td>10.3%</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>12.5%\textsuperscript{a}</td>
<td>1.7\textsuperscript{b}</td>
<td>7.4%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Palm et al 2016, \textsuperscript{b}Chhabra et al 2011, \textsuperscript{c}Loza et al 2012, \textsuperscript{d}Tasoglou et al 2015.

Figure S5: Functional form used to estimate aerosol yields for unspeciated compounds similar to the method used in Donahue et al.\textsuperscript{10} Grey shaded region indicates range of a factor of three in estimated yields.

SOA formation measurement.

A detailed description of the OFR measurements during this field study can be found in Palm et al.\textsuperscript{11}; a brief summary is presented here. \textit{In situ} SOA formation was measured by the AMS and a scanning mobility particle sizer (SMPS) after OH oxidation of ambient air inside the OFR. The maximum amount of SOA formation was observed after 0.4–1.5 equivalent days of OH aging.
(assuming a typical ambient OH concentration of $1.5 \times 10^6$ molec m$^{-3}$). On average in this photochemical age range, $0.93 \, \mu g\, m^{-3}$ SOA (2.4 $\mu g\, m^{-3}$ total SOA) was formed from the precursors in ambient air. This number includes a correction to account for the fate of condensable organic vapors in the OFR (referred to as the “LVOC fate correction” in Palm et al., 2016). When LVOCs are formed by oxidation in the OFR, they can have several fates, including condensing on existing particles to form SOA, condensing on the internal OFR walls (similar to chamber wall losses), being oxidized again prior to condensation leading to volatile fragmentation products, or exiting the OFR to condense rapidly on sampling line walls. The latter three fates do not result in SOA formation. In the atmosphere, the dominant fate of such condensable gases is condensation onto aerosols to form SOA. This correction is thus applied in order to relate the OFR measurements to what would occur in the atmosphere. This model was verified using sulfate aerosol formation from SO$_2$ during this study. The average overall correction factor is 1.8x.

**TD-EIMS calibration and analysis.**

The specific instrumental calibration and analysis procedures used in the BEACHON-RoMBAS field campaign are discussed in detail elsewhere for all instruments with the exception of the TD-EIMS. The TD-EIMS instrument is described by Cross et al., but a set of new calibration and data-processing routines were developed for the present campaign; these are discussed in this section.

*Mass concentration calibration.* To compute the total mass of S/IVOCs in a given mass spectrum, the sum of organic ion counts for a given data point was computed, and an analogous sum computed for a measurement of background signal (zero air). For unit-mass resolution data,
有机信号被分离来自无机信号通过应用一个滤波器到数据来排除离子在质量-电荷比主要为无机（例如，m/z 28, 32, 40, 44）。背景信号被从样品信号中排除，且离子计数的差值被乘以一个通过实验测量的比例常数来转换为总质量。这个实验测量是通过将一个化合物（n-十六烷或α-蒎烯）以已知速率蒸发到样品气流中使用移液泵或扩散室来实现的。对于移液泵，流量率和流体率都是已知的，允许准确的计算气相浓度。扩散室是一个涂有给定校准的毛细管；压力被施加到毛细管的一端，结果是饱和蒸汽的控制流，其速率被流量计测量，或根据泊肃叶方程计算。校准使用至少三个气相浓度来检查线性。图S6a中展示了在活动期间采取的典型校准图。实验室校准发现观察到的线性性可以延伸到更低的浓度。

图S6：样品TD-EIMS校准运行。面板a：确定有机质量从有机离子计数的校准。已知浓度被引入到仪器中使用扩散室n-十六烷和移液泵α-蒎烯。校准常数（斜率）包括收集和传输效率，对于使用校准参数中的两个分子是相同的。面板b：挥发性校准，相关c*到脱附时间，使用一个标准n-烷烃混合物。这些分子的已知饱和蒸气浓度可以通过线性拟合进行插值，获得材料在任何时间/温度下蒸发的估计。
Volatility calibration. To compute S/IVOC mass as a function of volatility, individual desorptions are split into bins computed using measured a standard mixture of n-alkanes (C_{10} - C_{28}) with known saturation vapor pressures. The relationship between desorption time and log(c*), shown in Fig. S6b, is linear; because the temperature ramp is itself linear, equivalent bin boundaries can be drawn in both temperature and time space. Conversion to c* bins involves integrating between the boundaries and subtracting an appropriate background (discussed further below). The measured desorption times/temperatures are likely a function of the sorption characteristics as well as the vapor pressure of a given molecule, and therefore the reported c* values are in alkane-equivalent volatilities.

Processing routines for high-resolution mass spectrometric data. The data analysis procedures for the TD-EIMS use the Squirrel and Pika modules (http://cires1.colorado.edu/jimenez-group/wiki/index.php/ToF-AMS_Analysis_Software). Separation of organic and inorganic ions is greatly simplified, since individual ions can be quantified within a single nominal mass (e.g. CO_{2}^{+} and C_{2}H_{4}O^{+} at m/z = 44). Since the composition of individual ions is known, elemental analysis is possible by summing the total signal for carbon, hydrogen, oxygen and nitrogen for all ions, a procedure that has been described in the literature^{24}. The correction factors described in Aiken et al. (accounting for systematic undercounting of oxygen due to electronegativity) have not been measured for the TD-EIMS. The TD-EIMS is also unable to quantify CO_{2}^{+} due to significant gas-phase interference. Together, these two effects likely lead to an estimate of the O/C that may be biased somewhat low. Elemental analysis is performed using the same approach for summation and background subtraction as the determination of organic mass, described below.
Background subtraction. Background subtraction procedures involve the subtraction of an appropriate thermogram for an S/IVOC-free air sample (zero air). Blank thermograms are taken at least twice a day to check for zero-drift and the possibility of accumulation of low-volatility material. At least two blank desorption runs are taken in succession in order to assess variability. Blank subtraction was performed in time space during BEACHON-RoMBAS.

Several additional steps are necessary to maximize the quality of the resulting data, shown in Figure S7. The first is that the tungsten filament is subject to rapid erosion, significantly increasing emission current over the course of the day, and thereby affecting the ionization efficiency (number of ions produced per microgram of sample). To counteract this, a calibration for signal as a function of emission current was performed (Figure S7a), and the fit function used to normalize all data points to an emission current of 1.0 mA (matched to the value used for the mass calibration). The second is that the signal intensity fluctuates from desorption to desorption independently of the emission current and independently of the total organic loading. The initial part of each desorption is entirely due to air ions, and should be essentially identical in all desorptions. Sample desorptions are therefore normalized such that the air signal matches that of the blank desorption, shown in Figure S7b, region 1. These corrections are on the order of 5%.

The last issue is that due to irregularities in the triggering and recording of mass spectra, the desorptions have a small random offset of up to 5 seconds. The offset is difficult to separate from real differences in the desorption, and can lead to large changes in the apparent volatility distribution if not accounted for, especially around sharp peaks (see Figure S7b, region 2). We use siloxanes as an internal standard due to their narrow peak shape and consistent profile, allowing for the correction for the time offset (Figure S7c). By correlating m/z 73 (dominated by siloxanes) for the sample and blank desorptions, and applying a peak finding routine to the
resulting profile (Figure S7d), the offset can be determined and applied to the blank run, allowing for an accurate background subtraction (black curve in Figure S7b). Differences between signal in different background measurements (summed across all volatility bins) was on the order of 0.1 μg/m³, so are unlikely to affect averaged results.

**Figure S7:** Details of TD-EIMS background subtraction. Panel a: differences in filament emission current over time are compensated for using the argon signal calibration shown. Panel b: a measured background desorption (blue curve) is normalized to a part of the ambient desorption (red curve) containing mostly inorganic ions (region 1). Panel c: Differences in run-to-run desorption times are found using siloxanes (m/z 73) as an internal standard. Panel d: the convolution of m/z 73 between background and ambient desorptions gives the time offset necessary to optimize background subtraction (black curve in panel b).
References.


7. Seinfeld, J. H. & Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to*


