

1 **Wintertime aerosol chemical composition, volatility, and spatial variability in the greater**
2 **London area**

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28 **Abstract**

29 The composition of PM₁ (particulate matter with diameter less than 1µm) in the greater
30 London area was characterized during the Clean Air for London (ClearfLo) project in winter 2012.
31 Two High-Resolution Time-of-Flight Aerosol Mass Spectrometers (HR-ToF-AMS) were
32 deployed at a rural site (Detling, Kent) and an urban site (North Kensington, London). The
33 simultaneous and high-temporal resolution measurements at the two sites provide a unique
34 opportunity to investigate the spatial distribution of PM₁. We find that the organic aerosol (OA)
35 concentration is comparable between the rural and urban sites, but the contribution from different
36 sources is distinctly different between the two sites. The concentration of solid fuel OA at the
37 urban site is about twice as high as at the rural site, due to elevated domestic heating in the urban
38 area. While the concentrations of oxygenated OA (OOA) are well-correlated between the two sites,
39 the OOA concentration at the rural site is almost twice that of the urban site. At the rural site, more
40 than 70% of the carbon in OOA is estimated to be non-fossil, which suggests that OOA is likely
41 related to aged biomass burning considering the small amount of biogenic SOA in winter. Thus, it
42 is possible that the biomass burning OA contributes a larger fraction of ambient OA in wintertime
43 than what previous field studies have suggested.

44 A suite of instruments was deployed downstream of a thermal denuder (TD) to investigate
45 the volatility of PM₁ species at the rural Detling site. After heating at 250°C in the TD, 40% of the
46 residual mass is OA, indicating the presence of non-volatile organics in the aerosol. Although the
47 OA associated with refractory black carbon (rBC, measured by a soot-particle aerosol mass
48 spectrometer) only accounts for <10% of the total OA (measured by a HR-ToF-AMS) at 250°C,
49 the two measurements are well-correlated, suggesting that the non-volatile organics have similar
50 sources or have undergone similar chemical processing as rBC in the atmosphere. Although the
51 atomic O:C ratio of OOA is substantially larger than that of solid fuel OA and hydrocarbon-like
52 OA, these three factors have similar volatility, which is inferred from the change in mass
53 concentration after heating at 120°C. Finally, we discuss the relationship between the mass fraction
54 remaining (MFR) of OA after heating in the TD and atomic O:C of OA and find that particles with
55 a wide range of O:C could have similar MFR after heating. This analysis emphasizes the
56 importance of understanding the distribution of volatility and O:C in bulk OA.

57 **1 Introduction**

58 Particulate matter (PM) concentration in the greater London area often exceeds European
59 air quality limits, causing adverse effects on the health of habitants in this area (Harrison et al.,
60 2012; Bohnenstengel et al., 2014). Therefore, it is critical to identify the PM sources in order to
61 implement effective strategies to control ambient pollutants. The Clean Air for London (ClearfLo)
62 project aimed to study boundary layer pollution in the greater London area through comprehensive
63 measurements of meteorology, gaseous and particulate composition (Bohnenstengel et al., 2014).
64 Multiple monitoring sites were set up in both urban and rural areas around London to quantify the
65 urban increment in gas-phase and particle-phase pollutants.

66 Previous studies in the greater London area have repeatedly shown that the concentration
67 of elemental carbon (EC) is higher in urban sites than rural sites due to elevated levels of primary
68 emissions such as vehicle exhaust and wood smoke (Crilley et al., 2015; Yin et al., 2015). The
69 origin of organic carbon (OC) at urban and rural sites is instead more challenging to elucidate
70 considering the myriad of different OC sources. Based on the ratios among multiple tracers (e.g.,
71 EC/OC and levoglucosan/OC) from different sources, Crilley et al. (2015) estimated that the
72 concentration of primary OC from vehicle emissions was higher in an urban area compared to a
73 rural area in the UK. Many studies have applied the Chemical Mass Balance (CMB) model for OC
74 apportionment (Yin et al., 2010; Crilley et al., 2015; Yin et al., 2015). However, due to the
75 uncertainties in the source profiles and the number of organic tracers included in the model, the
76 concentration of secondary OC is highly uncertain. In addition, OC measurements based on filter
77 samples on a daily basis limit the temporal resolution of rural vs. urban comparisons.

78 Factor analysis via Positive Matrix factorization (PMF) of aerosol mass spectrometer
79 (AMS) measurements is another widely used method to identify sources of organic aerosol (OA)
80 (Jimenez et al., 2009; Lanz et al., 2007; Ng et al., 2010; Xu et al., 2015a). Based on factor analysis
81 of AMS measurements around the world, Zhang et al. (2007) observed that the contribution of
82 hydrocarbon-like OA (a surrogate for primary OA) to total OA decreased from urban sites to rural
83 sites, but the oxygenated OA (a surrogate for secondary OA), showed the opposite trend. The
84 authors also showed that the average OA concentration is substantially lower in rural sites than
85 urban sites (2.8 vs. 7.6 $\mu\text{g m}^{-3}$). However, the trend observed in Zhang et al. (2007) needs to be

86 further verified since the urban vs. rural comparisons are not based on simultaneous measurements
87 between paired locations.

88 Comparison based on simultaneous measurements between different sites, especially
89 between rural and urban sites, is useful to identify regional and local sources of OA. For example,
90 by comparing concurrent AMS measurements of OA at multiple sites in the greater Atlanta area,
91 USA, Xu et al. (2015b) showed that the OA was spatially homogeneous and mainly regional in
92 summer, but the OA showed substantial spatial variability in winter. Based on PMF analysis of
93 AMS measurements, Crippa et al. (2013) investigated the correlation of various OA subtypes
94 between three urban sites located in a 20km-radius region in Paris, France during winter 2010. The
95 authors observed that the secondary OA factor had substantially better correlation between
96 different sites than the primary OA factors, including OA from vehicle, biomass burning, and
97 cooking. However, a rural vs. urban comparison was not performed in Crippa et al. (2013).

98 In addition to OA sources, the volatility of OA is an important property since it directly
99 determines the gas/particle partitioning. The thermal denuder (TD) has been used widely to
100 measure the aerosol volatility (An et al., 2007; Huffman et al., 2008; Saleh et al., 2011a). Many
101 previous studies inferred the volatility from the mass fraction remaining (MFR) or volume fraction
102 remaining (VFR), which is calculated as the ratio of the species mass (or volume) concentration
103 after heating to an elevated temperature in the TD to the species mass (or volume) concentration
104 without heating (An et al., 2007; Huffman et al., 2009b; Jonsson et al., 2007; Lee et al., 2011;
105 Stanier et al., 2007; Grieshop et al., 2009b; Xu et al., 2014; Huffman et al., 2009a). Larger MFR
106 is used as an indication for lower volatility of aerosol. However, Saleh et al. (2011b) suggested
107 that it is misleading to use MFR as an indication of volatility. This is mainly because the MFR is
108 an extensive parameter (which explicitly depends on the initial mass concentration) while aerosol
109 volatility is an intensive property (which depends only on chemical nature of the compounds in a
110 mixture). Instead of MFR, Saleh et al. (2011b) presented that that change in mass concentration
111 when reaching equilibrium upon heating (i.e., ΔC) is an appropriate measure of volatility.

112 Although multiple previous studies have investigated the volatility of laboratory-generated
113 OA (An et al., 2007; Huffman et al., 2009b; Jonsson et al., 2007; Lee et al., 2011; Stanier et al.,
114 2007; Grieshop et al., 2009b; Xu et al., 2014), there are only limited studies on the volatility of
115 ambient OA, especially on the volatility of OA from different sources (Hildebrandt et al., 2010;

116 Huffman et al., 2009a; Massoli et al., 2015; Paciga et al., 2015). Previous studies have showed the
117 presence of non-volatile organics in the ambient aerosol even after heating to high temperatures
118 (i.e., 230 - 300°C) (Huffman et al., 2009a; Häkkinen et al., 2012; Poulain et al., 2014; Massoli et
119 al., 2015; Liu et al., 2015). However, the sources of non-volatile organics are uncertain. Häkkinen
120 et al. (2012) and Poulain et al. (2014) found that the non-volatile residuals correlated with
121 anthropogenic tracers, such as BC and polycyclic aromatic hydrocarbons (PAHs), implying that
122 the non-volatile species are possibly linked to anthropogenic emissions. However, in both studies,
123 the thermal-denuder (TD) was only applied upstream of a scanning mobility particle sizer (SMPS);
124 therefore the composition of remaining compounds was not directly measured but only conjectured.
125 Massoli et al. (2015) coupled a TD with a soot-particle AMS (SP-AMS) during measurements in
126 California. The authors observed the existence of refractory OA (i.e., detectable via laser
127 vaporization in the SP-AMS, but not detectable by vaporization at 600°C in the standard AMS),
128 which was present in the fresh urban air masses, but not in the aged air masses.

129 Many studies have used the degree of oxidation of OA, such as atomic O:C ratio and
130 oxidation state (OS) as a proxy for volatility. For example, two oxygenated OA factors with high
131 but different O:C ratio are often resolved from PMF analysis on AMS data. These two oxygenated
132 OA factors are often named semi-volatile OOA (SVOOA) and low-volatility OOA (LVOOA)
133 based on the volatility inferred from O:C values (Ng et al., 2010; Huang et al., 2010; Mohr et al.,
134 2012; Jimenez et al., 2009). In a laboratory study on toluene SOA, Hildebrandt Ruiz et al. (2014)
135 observed a linear relationship between OS and effective saturation concentration of the aerosol.
136 However, for both ambient measurements and laboratory studies, it is uncertain whether the O:C
137 or OS of bulk OA is a good indicator of volatility. In Mexico City and Riverside, CA, Huffman et
138 al. (2009a) showed that the O:C ratio of the thermally-denuded OA increased with TD heating
139 temperature, which suggests that the O:C is inversely correlated with the volatility of organic
140 aerosol (i.e., the residual OA with lower volatility after heating has a higher O:C). In contrast, only
141 a weak correlation between O:C and volatility was observed in Hildebrandt et al. (2010), who
142 measured the volatility of ambient OA in Finokalia, Greece. The authors found that between
143 thermally-denuded OA and ambient OA, the mass spectrum was similar and the difference in f_{44}
144 (i.e., fraction of organic signal at m/z 44, which has a linear correlation with O:C) was not
145 statistically significant. This indicates that the degree of oxidation does not change after
146 evaporation of relatively volatile species. In addition, various relationships between O:C and

147 volatility (inferred from the MFR) have been observed in previous laboratory studies on different
148 SOA systems (Grieshop et al., 2009b; Qi et al., 2010; Donahue et al., 2012; Kroll et al., 2009;
149 Tritscher et al., 2011; Xu et al., 2014). For example, Xu et al. (2014) observed that while the O:C
150 of isoprene SOA formed in the laboratory without additional NO remained fairly constant (~0.6)
151 during photochemical aging, the VFR increased over time. Grieshop et al. (2009b) showed that
152 during photochemical aging, OA from wood fires became more oxidized (i.e., O:C increases), but
153 the MFR remained constant. Donahue et al. (2012) studied the photochemical aging of α -pinene
154 ozonolysis SOA and observed that while the OA became more oxidized (i.e., O:C increases), the
155 VFR decreased with aging. The authors proposed that the photochemical aging produced both
156 relatively volatile products and more oxidized products, which broadened the volatility distribution
157 of the OA (Donahue et al., 2012). In summary, while SOA becomes progressively more oxidized
158 (i.e., O:C increases) during aging, the MFR or VFR exhibits different trends (i.e., increases, stays
159 constant, or decreases over time) for different SOA systems.

160 In this study, we performed simultaneous measurements at a rural site (Detling, Kent) and
161 an urban site (North Kensington, London) in the greater London area in winter 2012 using two
162 Aerodyne high resolution time-of-flight mass spectrometers (HR-ToF-AMS) (DeCarlo et al.,
163 2006). The comparison of the simultaneous, high temporal resolution measurements and the OA
164 source apportionment by PMF analysis provide insights into sources of wintertime OA in the
165 greater London area. Since biogenic emissions are low in winter, these measurements allow a more
166 direct evaluation of the contributions of anthropogenic emissions to OA formation. We also
167 deployed a thermal denuder upstream of a suite of instruments to directly characterize the non-
168 volatile residual at 250°C. Furthermore, we investigated the volatility of different OA sources and
169 systematically evaluated the relationship between O:C and OA volatility.

170 **2 Method**

171 2.1 Sampling sites and meteorological conditions

172 Measurements were performed as part of the Clean Air for London (ClearfLo) project. An
173 overview of the ClearfLo field campaign can be found in Bohnenstengel et al. (2014). The main
174 goal of the ClearfLo project was to study boundary layer pollution in the greater London area by
175 comprehensive measurements of meteorology, gaseous- and particulate composition. Multiple

176 monitoring sites were set up in both urban and rural areas and at different elevations (street and
177 elevated level) to perform year-long measurements across London. In addition, two intensive
178 observation periods (IOPs) were conducted during winter (January-February, 2012) and summer
179 (July-August, 2012). Data presented in this paper were collected at the Detling site and the North
180 Kensington (NK) site during the winter IOP. Figure 1 shows the locations of both sites. The NK
181 site (51.521055°N, 0.213432°W) is an urban background site located in a residential area, 7 km to
182 the west of central London. The Detling site (51.301931°N, 0.589494°E) is a rural site located on
183 a plateau (200 m a.s.l.), 45 km southeast of London. The closest road is about 150m (south), which
184 carries ~42,000 vehicles per day (www.dft.gov.uk/traffic-counts). The typical meteorological data
185 (temperature, relative humidity, and wind speed) at the Detling site are shown in Fig. S1a. The
186 campaign-average temperature was 6°C. In the diurnal variation, the highest temperature was ~8°C
187 at 14:00 and the lowest temperature was ~5°C at 07:00. The relative humidity was 83% on average.
188 The wind speed was 5.8 m s⁻¹ on average, but it reached 10 m s⁻¹ occasionally. The wind rose plot
189 is shown in Fig. S1b. The prevailing wind was from the northeast and the southwest.

190 2.2 Instrumentation

191 In the following discussions on instrumental setup and data analysis methods, we will focus
192 on the rural Detling site. For instruments deployed at the urban NK site, only the high-resolution
193 time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne) ambient measurements are
194 included in this study. The data analysis of HR-ToF-AMS at the urban site is similar to that at the
195 rural site, which will be discussed below. Details regarding the measurements at the NK site can
196 be found in Young et al. (2015a).

197 A suite of instruments was deployed at the Detling site to characterize both the gas-phase
198 and particle-phase composition. Instruments of interest to this study are shown in Fig. S2 and are
199 described below. Ambient particles were sampled through a PM_{2.5} cyclone and then directed
200 through either a thermal denuder (denoted as TD line) or bypass line (denoted as bypass line)
201 before being analyzed by downstream instruments. The thermal denuder (TD, Aerodyne),
202 designed based on Huffman et al. (2008), consists of a 22" long stainless steel tube operated at
203 elevated temperatures (i.e., heated section), followed by a 24" section of activated charcoal held
204 at room temperature to adsorb the evaporated components from particles. The heating section was
205 operated at 120 and 250°C. The aerosol residence time in the heating section of the TD was 5.3 s

206 at the experimental flowrate rate (2.3 LPM determined by the sampling rate of instruments
 207 downstream of the TD). Caution is required when comparing the results between different studies
 208 with a TD because the TD configuration and residence times can be different. Particle loss in the
 209 TD was characterized based on the single particle soot photometer (SP2) refractory black carbon
 210 (rBC) mass measurement during the field campaign, since rBC does not evaporate even at 250°C.
 211 The transmission efficiency of TD is about 90% (Fig. S3), similar to the values reported in previous
 212 studies with similar TD configurations (Huffman et al., 2008; Massoli et al., 2015). The time scale
 213 to reach thermodynamic equilibrium in a given TD depends on a number of factors, such as TD
 214 temperature, aerosol mass concentration, aerosol diameter, and mass accommodation coefficient
 215 (Riipinen et al., 2010; An et al., 2007; Saleh et al., 2011b). In this study, we calculate the
 216 characteristic time for aerosol equilibration by following the algorithm in Saleh et al. (2011b). To
 217 evaluate the equilibration time scale in the TD, the authors started with the mass transfer equation
 218 (Eq. (1)) and then obtained the characteristic time for aerosol equilibration (τ in Eq. (2)) by
 219 performing dimensional analysis.

$$220 \quad \frac{dC_a}{dt} = -2\pi d_p DFN_{tot} (KC_{g,sat} - C_g) \quad \text{Eq. (1)}$$

$$221 \quad \tau = \frac{1}{2\pi d_p DFN_{tot}} \quad \text{Eq. (2)}$$

$$222 \quad F = \frac{1 + Kn}{1 + 0.3773Kn + 1.33Kn(1 + Kn) / \alpha} \quad \text{Eq. (3)}$$

223 In the equations, C_a , C_g , and $C_{g,sat}$ are the aerosol phase concentration, gas phase concentration, and
 224 gas phase saturation concentration, respectively. N_{tot} is the total number concentration, d_p is the
 225 particle size, D is the diffusion coefficient in the gas phase, K is the Kelvin effect correction, and
 226 F is the Fuchs-Sutugin correction, which is calculated by Eq. (3). In Eq. (3), Kn is the Knudsen
 227 number and α is the accommodation coefficient. D is on the order of $10^{-5} \text{ m}^2 \text{ s}^{-1}$ according to Tang
 228 et al. (2015) and α is on the order of 0.1 as shown in Saleh et al. (2011a). By using the campaign-
 229 average particle number concentration (i.e., $4.28 \times 10^3 \text{ cm}^{-3}$) and the mode of the particle number
 230 distribution (i.e., 87nm) in our study, we estimate that the characteristic equilibration time is about
 231 1600s, which is orders of magnitude longer than that residence time (5s) in the TD. Since the

232 evaporation process is likely far away from equilibrium, the gas phase saturation ratio is small and
233 the particles are likely evaporating in a vapor-free environment. Under this assumption, the gas
234 phase vapor concentration (i.e., C_g) in the mass transfer equation (Eq. (1)) can be neglected. After
235 integration over the residence time in the TD, the change in mass concentration upon heating (ΔC_a)
236 can be calculated by Eq. (4), in which $t_{\text{residence}}$ is the residence time in TD and the $\overline{C^*}$ is the
237 evaporation-time-averaged saturation concentration. Thus, the ΔC_a for each component is
238 proportional to its $\overline{C^*}$ because the other parameters are the same assuming the compounds are
239 internally mixed.

$$240 \quad \Delta C_a = C_{t=0} - C_{t_{\text{residence}}} = \int_0^{t_{\text{residence}}} \frac{KC_{g,\text{sat}}}{\tau} dt = \frac{t_{\text{residence}}}{\tau} K \overline{C^*} \quad \text{Eq. (4)}$$

241 A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne), a
242 soot-particle aerosol mass spectrometer (SP-AMS, Aerodyne), a single particle soot photometer
243 (SP2, DMT), and a scanning mobility particle sizer (SMPS, TSI) were placed downstream of the
244 TD. These four instruments alternated between sampling the bypass line (i.e., ambient) and the TD
245 line (i.e., thermally-denuded) every 10 min. When the instruments were sampling through the
246 bypass line, the heating section of TD was adjusted to the subsequent temperature setpoint. The
247 MFR was determined by comparing the measurements between bypass line and TD line.

248 The HR-ToF-AMS provides real-time measurements of the chemical composition and size
249 distribution of submicron non-refractory species (NR-PM₁) and has been described in detail
250 previously (Canagaratna et al., 2007; DeCarlo et al., 2006). In brief, the HR-ToF-AMS samples
251 particles through an aerodynamic lens and then impacts the focused particle beam on a heated
252 tungsten surface (~600°C). The resultant vapors are ionized by electron impact ionization and the
253 ions are analyzed using time-of-flight mass spectrometry. We used the ambient gas-phase CO₂
254 concentration (measured by a LI-COR CO₂ gas analyzer with 1 min resolution) to correct for the
255 gas-phase interference in the particle-phase CO₂⁺ signals for both the bypass line and TD line. The
256 assumption behind this correction for the TD line is that the CO₂ generated in the TD, if it exists,
257 is negligible. Unless otherwise specified, the elemental ratios, such as atomic O:C and H:C, were
258 calculated based on the latest recommendation by Canagaratna et al. (2015), who modified the
259 original method developed for the HR-ToF-AMS (Aiken et al., 2007; Aiken et al., 2008). The HR-

260 ToF-AMS data were analyzed using the standard AMS analysis toolkits SQUIRREL v1.56A and
261 PIKA v1.15.

262 The SP-AMS measures the chemical composition of rBC containing particles by using an
263 intracavity laser vaporizer (1064 nm). The detailed working principles of SP-AMS are extensively
264 discussed in Onasch et al. (2012). In brief, after being focused through an aerodynamic lens, the
265 rBC-containing particles are heated and vaporized by laser absorption. The chemical composition
266 of both the rBC and any associated coatings are analyzed via high-resolution mass spectrometry.
267 The SP-AMS data presented in this paper were obtained between 5 and 15 February, 2012, when
268 the instrument was operated in the laser vaporizer only configuration, that is, only rBC-associated
269 species were detected. Analysis and interpretation of the SP-AMS measurements for the entire
270 deployment at Detling are presented in Williams et al. (2015).

271 The single particle soot photometer (SP2) measures rBC using laser-induced
272 incandescence. The method has been described previously (Schwarz et al., 2006; Stephens et al.,
273 2003). In brief, a 1064 nm Nd:YAG laser irradiates the particles as they enter the SP2, where upon
274 vaporization and incandescence is induced in the particles containing rBC. The incandescence
275 signal is proportional to the mass of rBC per particle, and with the sampling volume, rBC mass
276 concentrations are quantified. The SP2 at the Detling site was calibrated using fullerene soot (Alfa
277 Aesar, Inc., Ward Hill, Massachusetts; Stock# 40971, Lot# L18U002). Fullerene soot is an rBC
278 surrogate used for calibration of the SP2 due to its known density and similarities to ambient rBC
279 (Baumgardner et al., 2012; Laborde et al., 2012). Data analysis was performed with the Paul
280 Scherrer Institut Toolkit (PSI, Martin Gysel) developed for SP2 analysis within Igor Pro
281 (Wavemetrics, Inc.).

282 2.3 Collection efficiency of the HR-ToF-AMS

283 In order to provide quantitative data from HR-ToF-AMS measurements, the particle
284 collection efficiency (CE), which is largely due to particles bouncing on the vaporizer, needs to be
285 evaluated. For the bypass line, we calculated the CE based on the composition-dependent
286 algorithm proposed by Middlebrook et al. (2012) (i.e., CDCE). The CDCE for the bypass line
287 ranges from 0.45 to 0.97, with the campaign-averaged value 0.52 ± 0.08 (one standard deviation).
288 In order to validate the application of CDCE, we converted the mass concentrations of ambient

289 non-refractory species measured by HR-ToF-AMS (after CDCE correction) together with the mass
290 concentration of refractory species (i.e., rBC and crustal material) to volume using Eq. (5) and then
291 compared the calculated volume with SMPS measurements.

$$292 \quad \text{volume} = \frac{[\text{NO}_3^-] + [\text{SO}_4^{2-}] + [\text{NH}_4^+]}{1.75} + \frac{[\text{Cl}^-]}{1.52} + \frac{[\text{org}]}{\rho_{\text{org}}} + \frac{[\text{crustal material}]}{2.7} + \frac{[\text{BC}]}{0.73} \quad \text{Eq. (5)}$$

293 In Eq. (5), 1.75 g cm⁻³ was used as the density for inorganic nitrate, sulfate, and ammonium,
294 and 1.52 g cm⁻³ was used as the density for chloride (Poulain et al., 2014). The density of ambient
295 organics was estimated using atomic O:C and H:C ratios as suggested by Kuwata et al. (2012). It
296 is noted that the O:C and H:C ratios calculated based on Aiken et al. (2008) were used in the
297 density estimation in order to be consistent with Kuwata et al. (2012). The organic density was
298 estimated to be 1.30, 1.42 and 1.68 g cm⁻³ for bypass line, TD = 120°C and TD = 250°C,
299 respectively. The estimated density values were within the literature range (Hallquist et al., 2009).
300 The concentration of crustal material was estimated by summing the normal oxides (Na₂O, MgO,
301 Al₂O₃, SiO₂, CaO, K₂O, FeO, Fe₂O₃, and TiO₂) of tracer elements (Malm et al., 1994). The tracer
302 elements were measured by PM_{1.0-0.3} rotating drum impactors and analyzed by synchrotron
303 radiation-induced X-ray fluorescence spectrometry (Visser et al., 2015). The density of crustal
304 material (2.7 g cm⁻³) was adapted from Lide (1991). The rBC concentration was measured by the
305 SP2. For the rBC density, many previous studies have used 1.77 g cm⁻³ (Salcedo et al., 2006;
306 Poulain et al., 2014; Huffman et al., 2009a). However, we note that 1.77 g cm⁻³ (adapted from Park
307 et al. (2004)) is the inherent material density of diesel soot particles. If the inherent material density
308 is used, one needs to consider the non-sphericity of rBC when comparing the calculated volume
309 to the SMPS volume as the particles are assumed to be spherical when estimating the SMPS
310 volume. In order to circumvent this issue, we used an effective density of rBC in this study. Park
311 et al. (2003) measured the effective density of diesel soot particles in the 50-300nm range (mobility
312 diameter) by using a Differential Mobility Analyzer - Aerosol Particle Mass analyzer (DMA -
313 APM) system. The soot particles were firstly classified based on mobility diameter in DMA and
314 the mass of classified particles was then measured by APM. The effective density was calculated
315 with the following equation by assuming spherical particles:

316

$$\rho_{\text{eff}} = \frac{\text{mass}}{\frac{\pi}{6} d_{\text{me}}^3} \quad \text{Eq. (6)}$$

317 where d_{me} is the mobility equivalent diameter. Thus, applying the effective density measured by a
 318 DMA-APM system allows one to convert BC mass to its apparent volume, which is comparable
 319 to the SMPS volume. One factor that complicates the choice of rBC effective density is that this
 320 value decreases with increasing mobility diameter as shown in Park et al. (2003). Limited by the
 321 lack of knowledge of the size distribution (mobility diameter based) of rBC in our data, we
 322 calculated the average effective density based on all the values reported in Park et al. (2003) and
 323 used this average value (0.73 g cm^{-3}) in our study. This simplification is reasonable considering
 324 the following reasons. Firstly, Crilley et al. (2015) estimated that 70% of rBC at the Detling site is
 325 from traffic, which is similar to the BC types in Park et al. (2003). Secondly, the size distribution
 326 of total particles measured by SMPS in our study largely overlapped the size range studied in Park
 327 et al. (2003).

328 The calculated volume (based on HR-ToF-AMS + rBC + crustal material) was then
 329 compared with co-located SMPS measurements (Fig. 2). The SMPS measured the particle number
 330 distribution between 15.1 and 532.8 nm mobility diameter. The number distribution can be
 331 converted to a volume distribution assuming spherical particles. On average, the difference
 332 between the calculated volume and the SMPS volume was within 6%, which validates the
 333 application of CDCE for the bypass line (Fig. 2a).

334 However, the CDCE is not applicable for the TD line because the CDCE algorithm is
 335 parameterized based on aerosol neutralization (Eq. (7)), which depends strongly on the accuracy
 336 of the ammonium concentration measurement. The ammonium concentration decreased quickly
 337 upon heating and was close to the instrument detection limit at 250°C . Thus, we evaluated the CE
 338 for the TD line by comparing the calculated volume (based on HR-ToF-AMS + rBC + crustal
 339 material) and the SMPS volume (Salcedo et al., 2006).

$$\text{neutralization} = \frac{\text{NH}_{4,\text{meas}}}{\text{NH}_{4,\text{predict}}} = \frac{\text{NH}_{4,\text{meas}}}{18 \times \left(\frac{\text{SO}_4 \times 2}{96} + \frac{\text{NO}_3}{62} + \frac{\text{Chl}}{35.5} \right)} \quad \text{Eq. (7)}$$

341 We noted that the selection of the rBC density has a substantial effect on the TD line CE. For
342 example, varying the rBC density from 1.77 to 0.60 g cm⁻³ (i.e., from the inherent material density
343 to the effective density of 100 nm diesel soot particle reported in Park et al. (2003)) changed the
344 CE at 250°C by a factor of 2 (Table S1). This sensitivity analysis highlighted the importance of
345 the rBC density in applying this method to evaluate CE, especially for the TD line where rBC
346 accounted for a large fraction of the mass concentration. In this study, since the TD line CE
347 calculated with an rBC effective density of 0.73 g cm⁻³ (i.e., average value from Park et al. (2003))
348 was close to the default value for CE (i.e., 0.45), we used 0.45 as the TD line CE in our analysis.
349 As shown in Fig. 2b and 2c, the default CE results in a reasonable agreement between the
350 calculated volume and the SMPS volume for the TD line. Specifically, the differences between the
351 calculated volume and the SMPS volume are 14% and 11% at 120°C and 250°C, respectively,
352 which are within the range of measurement uncertainties. Future studies are warranted to
353 comprehensively investigate the change of AMS CE after heating of the aerosol.

354 2.3 Data analysis

355 2.3.1 Positive matrix factorization (PMF) analysis

356 Positive Matrix Factorization (PMF) analysis has been widely used for aerosol source
357 apportionment in the AMS community. This technique represents the observed data as a linear
358 combination of factors with constant mass spectra but varying concentrations across time in the
359 dataset (Paatero and Tapper, 1994; Paatero, 1997). Two solvers have been used for PMF analysis
360 of AMS data, PMF2 and the multilinear engine (ME-2). The PMF2 solver does not require a priori
361 information, which avoids some subjectivity. The ME-2 solver uses a priori information to reduce
362 rotational ambiguity among possible solutions (Canonaco et al., 2013; Paatero, 1999).

363 For the ambient OA measurements, we used the standard PMF2 solver, which does not
364 include any a priori information. This analysis is denoted as PMF_{ambient} and was performed using
365 the PMF Evaluation Toolkit (PET) software developed by Ulbrich et al. (2009). The error matrix
366 was pre-treated based on the procedure in Ulbrich et al. (2009). *m/z*'s with signal-to-noise ratio in
367 the range 0.2-2 were down weighted by a factor of 2, and *m/z*'s with signal-to-noise ratio smaller
368 than 0.2 were removed. Also, the contributions of O⁺, HO⁺, H₂O⁺, CO⁺ and CO₂⁺ were down
369 weighted to avoid excessive weighting of CO₂⁺ and related fragments. Following the detailed

370 procedure listed in Zhang et al. (2011), the PMF solutions were evaluated by investigating the key
371 diagnostic plots (Fig. S4), mass spectral signatures, correlations with external tracers, and the
372 diurnal profiles. The rotational ambiguity of the optimal solution was examined by changing the
373 FPEAK parameter from -1 to 1. In our case, an FPEAK value of 0 ($Q/Q_{\text{exp}} = 1.804$) was selected
374 because the correlations between factors and external tracers were not improved for FPEAK values
375 that were different from 0. We resolved three factors from $\text{PMF}_{\text{ambient}}$, i.e., hydrocarbon-like OA
376 (HOA), solid fuel OA (SFOA), and oxygenated OA (OOA), which are discussed in section 3.1.
377 The choice of a three-factor solution is discussed in detail in the SI (Fig. S5).

378 For the TD line measurements, we first tried the PMF2 solver on the combined ambient
379 and thermally-denuded OA spectra (denoted as $\text{PMF}_{\text{ambient+TD}}$); this is the same approach applied
380 in Huffman et al. (2009a). However, in this study, we encountered several issues in $\text{PMF}_{\text{ambient+TD}}$
381 analysis. The first issue we encountered is the “mixing” behavior of OA factors. For example, in
382 the three-factor solution of $\text{PMF}_{\text{ambient+TD}}$, one factor has similar fragmentation patterns as HOA
383 from $\text{PMF}_{\text{ambient}}$, but this factor also has substantial signal at $\text{C}_2\text{H}_4\text{O}_2^+$ (m/z 60, often used as a
384 tracer marker for SFOA) (Fig. S6). In addition, another factor from $\text{PMF}_{\text{ambient+TD}}$ has similar time
385 series as SFOA from $\text{PMF}_{\text{ambient}}$, but has similar mass spectrum as OOA from $\text{PMF}_{\text{ambient}}$. The
386 second issue we encountered is that the mass loading of the OOA factor is occasionally higher in
387 the TD runs compared to the preceding and succeeding bypass runs (Fig. S7). The reason for this
388 behavior is not clear, but it is likely caused by the fact that only highly oxidized species remain
389 upon heating and the mass spectrum of the remaining OA becomes more similar to the oxidized
390 OA factors. Thus, PMF analysis might overestimate the concentrations of the oxidized OA factor.
391 Overall, the PMF analysis on the combined bypass and TD line measurements by using the PMF2
392 solver without a priori information could not clearly separate OA factors. This is likely caused by
393 the fact that including the thermally denuded data might distort the PMF results by introducing
394 additional time variation in the mass spectra as pointed out by Huffman et al. (2009a).

395 Considering the above issues associated with $\text{PMF}_{\text{ambient+TD}}$, we performed PMF analysis
396 using the ME-2 solver on the TD line measurements by applying the factor profiles determined
397 from $\text{PMF}_{\text{ambient}}$ as a priori information, in order to improve the separation of OA factor. Data
398 obtained at 120°C and 250°C were analyzed separately in order to account for the variability of
399 factor mass spectra at different temperatures. The analyses for 120°C and 250°C are denoted as

400 ME-2_{120C} and ME-2_{250C}, respectively, and were performed using the toolkit Source Finder (SoFi
401 v4.8) (Canonaco et al., 2013). The error matrix was pre-treated in the same way as for PMF_{ambient}.
402 As recommended by Canonaco et al. (2013) and Crippa et al. (2014), secondary factors (i.e., OOA
403 factor) were unconstrained and primary factors (i.e., HOA and SFOA) were constrained with a
404 small a value (e.g., <0.1), which allows small variations of the resolved factors compared to the
405 anchor profile in order to account for differences in ambient sources and avoid a mixing situation.
406 We performed sensitivity tests and found that increasing the a value from 0 to 0.1 only reduced
407 the fitting “residual” (i.e., Q/Q_{exp}) by $<1\%$ and had negligible influence on the factor profiles and
408 factor concentrations (Figs. S8 and S9) for both ME-2_{120C} and ME-2_{250C}. Therefore, considering
409 that 1) the small effect of the a value, and 2) the fact that the anchor profiles of HOA and SFOA
410 resolved from PMF_{ambient} were clearly separated, we selected 0 as the a value, which fully
411 constrained the profile of HOA and SFOA. The mass spectra of thermally-denuded OOA at 120°C
412 and 250°C, which were not constrained in ME-2_{120C} and ME-2_{250C}, change slightly compared to
413 the ambient OOA mass spectrum (Fig. S10). The most discernable changes occur at f_{CHO^+} (i.e.,
414 fraction of organic signal at CHO^+), $f_{\text{C}_2\text{H}_3\text{O}^+}$ and $f_{\text{CO}_2^+}$, suggesting that the composition of OOA is
415 different at different denuding temperatures.

416 2.3.2 Retroplume analysis

417 Retroplume analysis was performed using the Numerical Atmospheric-Dispersion
418 Modelling Environment (NAME) dispersion model (Jones et al., 2007) to identify the origin of air
419 masses. The NAME model used the Unified Model reanalysis of meteorological data and
420 generated the surface level pathways of air masses arriving at the site after 1 day of transport (i.e.,
421 1-day footprints). The domain of influence of the NAME run was divided into a number of
422 geographical regions (i.e., Atlantic ocean, Benelux area, etc, shown in Fig. S11) as described in
423 Fleming et al. (2012). For each 3-hour period, the fraction of air masses arriving from each region
424 was calculated. According to Liu et al. (2013), for the time periods when the fraction of one region
425 is greater than the 40th percentile of that region’s air masses fraction, that region is deemed to have
426 a strong influence on the sampling site. Regions can also be grouped into broader sectors. In this
427 study, we focused on two broader sectors, the easterly sector (North France and Benelux area) and
428 the westerly sector (Atlantic and Ireland). It is important to note that sometimes the sampling site
429 is influenced by more than one sector.

430 In the following discussion, we first investigate the PM₁ composition and OA source
431 apportionment at the Detling site (section 3.1). Then in section 3.2, we compare the measurements
432 at the rural Detling site with the urban NK site to investigate the spatial variability of aerosol in
433 the greater London area. Lastly, we examine the aerosol volatility based on measurements at the
434 Detling site (section 3.3).

435 **3 Results and Discussion**

436 3.1 Aerosol characterization at the Detling site

437 Figure 3a shows the time series of PM₁ composition measured by HR-ToF-AMS (i.e., non-
438 refractory species) and SP2 (i.e., rBC). The campaign-average PM₁ concentration is $14 \pm 12 \mu\text{g m}^{-3}$
439 (average \pm one standard deviation). The chemical composition of PM₁ is dominated by nitrate
440 and organics, which on average accounts for 32% and 31% of total PM₁ mass, respectively. The
441 other components include sulfate (17%), ammonium (14%), rBC (4.3%), and chloride (2.2%).
442 Based on the fragmentation pattern of nitrate functionality in the AMS (i.e., NO⁺/NO₂⁺ ratio), one
443 can determine whether the nitrate is of organic or inorganic origin (Farmer et al., 2010; Boyd et
444 al., 2015; Fry et al., 2009; Xu et al., 2015b). At the Detling site, the measured NO⁺/NO₂⁺ ratio is
445 close to the value of pure ammonium nitrate (Fig. S12), indicating that the majority of the measured
446 nitrates are inorganic nitrates.

447 The PMF analysis on the ambient organic mass spectra (i.e., PMF_{ambient}) resolves three OA
448 subtypes: oxygenated organic aerosol (OOA), solid fuel organic aerosol (SFOA), and
449 hydrocarbon-like organic aerosol (HOA), which accounts for 54%, 23%, and 19% of total OA,
450 respectively. The time series and mass spectra of the three factors are shown in Fig. 4. HOA is
451 representative of primary OA from vehicle emissions as its mass spectrum is dominated by
452 hydrocarbon-like ions (i.e., C_xH_y⁺ ions). HOA is correlated with rBC and NO_x (Fig. 4a). SFOA is
453 a surrogate for fresh OA from solid fuel combustion, including biomass burning (Young et al.,
454 2015b). The mass spectrum of SFOA is characterized by prominent signals at C₂H₄O₂⁺ (*m/z* 60)
455 and C₃H₅O₂⁺ (*m/z* 73), which are likely fragments from anhydrosugars such as levoglucosan and
456 mannosan (tracers for biomass burning). The time series of SFOA correlates with particle-phase
457 nitrated phenol compounds (Mohr et al., 2013), which are mainly associated with coal and wood
458 combustion (Fig. 4b). OOA is the most oxidized (O:C = 0.92) among all three factors. At the

459 Detling site, the OOA time series shows a good correlation with sulfate (Pearson's $R=0.80$, Fig.
460 4a) and acetaldehyde ($R=0.78$, Fig. 4a). Acetaldehyde could arise from direct emissions, such as
461 fossil fuel combustion and biomass burning, and secondary production by oxidation of various
462 hydrocarbons (Langford et al., 2009). The observation that acetaldehyde correlates better with
463 OOA than SFOA ($R = 0.78$ vs. 0.66) is consistent with previous studies which showed that
464 acetaldehyde is dominated by secondary production after hours of photochemical processing
465 (Hayes et al., 2013; Sommariva et al., 2011; de Gouw et al., 2005).

466 The identification of the sources of OOA is challenging because the mass spectrum of OA
467 from different sources becomes more similar and resembles that of OOA with increasing
468 photochemical aging (Ng et al., 2010; Jimenez et al., 2009). For the Detling data, we hypothesize
469 that OOA is mainly from aged biomass burning. Liu et al. (2015) combined the PMF results from
470 our study with radiocarbon analysis and estimated that 73-90% of carbon in the OOA factor was
471 non-fossil. Biogenic emissions and biomass burning are the major sources for non-fossil carbon.
472 The large fraction of non-fossil carbon indicates that the OOA measured at the Detling site largely
473 arises from aged biomass burning because the concentration of biogenic VOCs is low in winter
474 due to cold temperature and reduced photosynthesis. For example, Yin et al. (2015) showed that
475 the concentrations of isoprene SOA tracers (i.e., methyltetrols) and α -pinene SOA tracers (pinic
476 acid and pinonic acid) at the NK site during the winter IOP are only 0.5 ng m^{-3} and 2.3 ng m^{-3} ,
477 respectively, which are substantially lower than the concentrations measured at US and European
478 sites during warmer months. Both laboratory studies and ambient measurements have revealed
479 that the oxidation of biomass burning OA is a rapid process (Hennigan et al., 2011; May et al.,
480 2012; Bougiatioti et al., 2014; Zhao et al., 2015). During the oxidation process, the mass spectrum
481 of biomass burning OA could lose its characteristic signature (i.e., $\text{C}_2\text{H}_4\text{O}_2^+$ and $\text{C}_3\text{H}_5\text{O}_2^+$) and
482 becomes progressively similar to that of OOA (Grieshop et al., 2009a; Hennigan et al., 2011).
483 Thus, the aged biomass burning OA could be apportioned to the OOA by PMF analysis. With this,
484 it is possible that the biomass burning OA contributes a larger fraction of ambient OA in winter
485 than what previous field studies suggested, where this factor was typically identified based on the
486 presence of larger signals at $\text{C}_2\text{H}_4\text{O}_2^+$ (m/z 60) and $\text{C}_3\text{H}_5\text{O}_2^+$ (m/z 73) alone.

487 Figure 3b shows the aerosol composition when air masses come from the easterly sector
488 (i.e., mainland Europe) and the westerly sector (i.e., Atlantic Ocean). The concentration of PM_{10} is

489 five times higher for the easterly sector compared to the westerly sector. This is consistent with
490 previous studies which showed that elevated pollution levels in the southern UK were often
491 associated with heavily polluted air masses transported from mainland Europe (Charron et al.,
492 2013; Morgan et al., 2010; Morgan et al., 2015; Putaud et al., 2004). Similar to the greater London
493 area, Beekmann et al. (2015) found that 70% of fine PM in the Paris megacity was also largely
494 influenced by regional contribution from mainland Europe. A large fraction of OA from mainland
495 Europe is highly oxidized organic aerosol (i.e., OOA). For example, while the concentrations of
496 HOA and SFOA only double when the source of air masses switches from the Atlantic Ocean to
497 mainland Europe, the OOA concentration increases from $\sim 0.5 \mu\text{g m}^{-3}$ to $\sim 3 \mu\text{g m}^{-3}$ (Fig. 3b). The
498 higher contribution of OOA to total OA is consistent with the total OA from mainland Europe
499 being more oxidized than that from the Atlantic Ocean. In Fig. 5, we compare the OA oxidation
500 level for different air masses in the f_{44} (i.e., fraction of organic signal at m/z 44) vs. f_{43} (i.e., fraction
501 of organic signal at m/z 43) plot (Ng et al., 2010). The OA for the easterly sector has a higher f_{44}
502 compared to the westerly sector, suggesting that the air masses advected from mainland Europe
503 have undergone a larger extent of photochemical processing.

504 3.2 Comparison between London and Detling

505 In this section, we compare the two simultaneous HR-ToF-AMS measurements at the rural
506 Detling site and the urban NK site. Only the sampling periods (hourly basis) when both instruments
507 were operative from 20 January to 8 February, 2012 are included in the comparison, so that the
508 concentrations reported in this section are different from those reported in section 3.1, where the
509 whole data set at the Detling site (from 20 January to 15 February, 2012) is used.

510 3.2.1 Non-refractory species and OA factors comparison

511 The comparison between the Detling and NK sites in terms of concentration and diurnal
512 variation of the five NR-PM₁ species is shown in Fig. 6 and Fig. S13, respectively. The
513 concentration of nitrate is substantially higher at the urban NK site (i.e., $5.6 \mu\text{g m}^{-3}$) than the rural
514 Detling site ($3.5 \mu\text{g m}^{-3}$). This observation is consistent with McMeeking et al. (2012), who
515 performed airborne measurements in the urban London region and observed an enhancement of
516 nitrate concentration inside urban plumes. The elevated nitrate concentration (largely inorganic
517 nitrate) at the urban site suggests that nitrate has a strong local contribution, likely due to the fact

518 that nitrate formation occurs rapidly and its major sources (i.e., oxidation of NO_x) are much higher
519 over inner London (Shaw et al., 2015). The sulfate concentration is well correlated between two
520 sites ($R = 0.82$, Fig. 7), consistent with previous findings that sulfate has a strong regional
521 contribution in the greater London area (Harrison et al., 2012; Yin et al., 2010). However, the
522 sulfate concentration is about 60% higher at the rural Detling site than the urban NK site. The
523 comparison of sulfate concentration between the rural and urban site depends on the origin of air
524 masses. As shown in Fig. S14, the sulfate concentrations agree well between the two sites when
525 air masses come from Atlantic Ocean (i.e., westerly) compared to mainland Europe (i.e., easterly).
526 The reason for the elevated sulfate concentration at the rural site will be discussed below.

527 Although the average concentration of total OA is comparable between NK (i.e., $4.3 \mu\text{g m}^{-3}$)
528 and Detling ($4.0 \mu\text{g m}^{-3}$) (Fig. 6), PMF analysis reveals that the contribution to total OA from
529 different sources is distinctly different between the urban and rural sites. At the urban NK site,
530 primary OA sources, including cooking, vehicle emission, and solid fuel combustion, account for
531 about 70% of total OA. At the rural Detling site, in contrast, more than half of the total OA is aged
532 secondary OA (i.e., OOA). Specifically, the cooking OA (i.e., COA), which accounts for 18% of
533 total OA at the urban NK site, is not resolved at the rural Detling site. This is expected as there is
534 no cooking activity near the rural Detling site. Hydrocarbon-like OA (i.e., HOA) only shows weak
535 correlation between the two sites ($R = 0.53$) (Fig. 8f), which is because HOA is representative of
536 primary OA and it is influenced by local vehicle emissions. The SFOA time series is moderately
537 correlated ($R = 0.65$) between Detling and NK (Fig. 8d). The SFOA concentration at the urban NK
538 site is almost twice as high at the rural Detling site, which is likely due to the elevated domestic
539 space heating activities and related emissions in the urban London area during wintertime (Young
540 et al., 2015b; Crilley et al., 2015).

541 Among all three OA factors, the OOA factor has the strongest correlation between the two
542 sites ($R = 0.81$) (Fig. 8b), which suggests that OOA likely represents regional SOA. Crilley et al.
543 (2015) also observed that the filter-based daily-average OC concentration is well correlated ($R^2 >$
544 0.82) between Detling and NK sites during the same period as our study. However, the good
545 correlations of OOA and OC observed in our study and Crilley et al. (2015) are different from the
546 observation in Charron et al. (2013), where the authors found that secondary organic carbon (SOC)
547 was much less spatially homogeneous than nitrate and sulfate by comparing an urban (Birmingham

548 site) and a rural site (Harwell site) in the greater London area between July and November 2010.
549 The difference between this study and Charron et al. (2013) is likely due to the uncertainty in the
550 SOC estimation method. In Charron et al. (2013), SOC is estimated from filter measured total OC
551 by using the EC/OC method where a constant EC/CC ratio from primary sources is applied. As
552 discussed in Charron et al. (2013), their estimation and the weak correlation of OC between
553 different sites are affected by the uncertainties associated with the choice of source ratios and
554 analytical procedure. In addition to SOC estimation uncertainty, the differences in sampling sites,
555 sampling periods, and size cuts (PM_{2.5} vs. PM₁) between Charron et al. (2013) and our study could
556 also play a role.

557 Although the OOA is well-correlated between the two sites, the OOA concentration is
558 almost twice as high at the rural Detling site than the urban NK site (Fig. 6). This observation is
559 similar to the comparison of sulfate between the two sites, which is also usually considered to be
560 regional, as discussed above. Based on atmospheric chemistry transport model, the higher OOA
561 concentration at the rural site is a result of meteorological conditions, which cause a strong gradient
562 of SOA concentration when air masses are advected from polluted mainland Europe. For example,
563 to simulate the SOA formation in the winter IOP, Ots et al. (2015) applied the regional EMEP4UK
564 (European Monitoring and Evaluation Programme) model, which uses 5 km by 5 km British Isles
565 grid nested within 50 km by 50 km greater Europe domain, 21 vertical levels, Weather Research
566 and Forecasting (WRF) model meteorological reanalysis, and National Atmospheric Emissions
567 Inventory (NAEI) for the UK, Centre on Emission Inventories and Projections (CEIP) emissions
568 for other European countries. They observed a steep negative gradient of SOA concentration from
569 near European continent to southern England. The steep gradient is a result of meteorological
570 conditions (i.e., mainly wind direction), which causes that the pollution plume from mainland
571 Europe largely passes over the rural site, but not the urban site.

572 3.2.2 OA oxidation level

573 Figure 5 compares the OA oxidation level between Detling and NK. Compared to the NK
574 site, the average OA at the Detling site has higher f_{44} , indicating that the OA at the Detling site is
575 more oxidized than that at the NK site. The difference in OA oxidation level between the Detling
576 and the NK sites are due to different OA compositions. As shown in Fig. 6, the OA at the NK site
577 is dominated by primary OA (~70% of total OA) from cooking, vehicle emissions, and solid fuel

578 combustion, whose O:C is much lower than OOA. In contrast, more than half of OA at the Detling
579 site is OOA, which is highly oxidized.

580 3.3 Aerosol volatility analysis

581 3.3.1 Volatility of non-refractory species and OA factors

582 Figure 9a and c show the thermograms and the change in concentration after heating (ΔC)
583 of non-refractory (NR) species as measured by the HR-ToF-AMS. The MFR is calculated as the
584 ratio of the species mass concentration through the TD to the average mass concentration of the
585 preceding and succeeding bypass runs. The ΔC is calculated as the concentration difference
586 between the bypass and TD runs (Eq. (4)). Both the MFR and the ΔC have been corrected for the
587 particle loss in the thermal denuder (TD) by using the TD transmission efficiency as discussed in
588 section 2.2. The MFR of NR species is consistent with previous ambient measurements (Huffman
589 et al., 2009a). Nitrate has the largest average ΔC and the smallest MFR among all NR species. The
590 MFR of nitrate decreases to 0.15 at 120°C and it volatilizes completely at 250°C (i.e., MFR <
591 0.05). Sulfate is the least volatile species at 120°C, which has the smallest average ΔC and an MFR
592 equal to 0.89. The sulfate MFR is higher than that of ammonium sulfate from laboratory studies,
593 which has been attributed to particle mixing state affecting the sulfate volatility (Huffman et al.,
594 2009a; Massoli et al., 2015). For OA, the MFR is about 0.16 at 250°C. On average, 0.88 $\mu\text{g m}^{-3}$
595 OA remains after heating, implying the existence of non-volatile organic compounds. Figure 9d
596 shows that the ΔC 's of three OA factors are not statistically different at 120°C. This suggests that
597 although the O:C of OOA (O:C = 0.92) is substantially larger than that of HOA (O:C = 0.22) and
598 SFOA (O:C = 0.37), the volatilities of the three factors are similar at 120°C. Thus, the O:C may
599 not be a good indicator of the volatility of the OA factors. At 250°C, both HOA and SFOA fully
600 evaporate (MFR < 0.05) so that the volatility cannot be compared under this temperature.

601 3.3.2 Sources of residual organics at 250°C

602 Figure 10 shows the chemical composition of the residual PM_{10} after heating to 250°C. The
603 major components of the residual PM_{10} are OA (90% of OA is OOA), rBC, and sulfate. rBC
604 accounts for about 30% of the remaining mass. This value is smaller than that reported in Poulain
605 et al. (2014) (i.e., 47% in summer and 59% in winter for TD temperature 300°C) and in Häkkinen
606 et al. (2012) (i.e., 55-87% depending on season for TD temperature 280°C). The differences are

607 likely due to 1) the density of rBC used in previous studies when converting SMPS volume
608 concentration to mass concentration, 2) different TD temperatures and residence times, 3)
609 techniques to measure rBC concentration, and 4) sampling locations.

610 At 250°C, OA has the largest contribution (~40%) to the residual mass. The existence of
611 highly oxidized, non-volatile organic compounds is consistent with previous ambient
612 measurements and model studies. For example, Cappa and Jimenez (2010) used a kinetic model
613 to simulate the volatility of OA factors measured by Huffman et al. (2009a) in the MILAGRO
614 field campaign and the authors estimated that a large fraction of OA was non-volatile and would
615 not evaporate under any atmospheric conditions.

616 The sources of non-volatile organics are uncertain, but appear to be related to
617 anthropogenic emissions. A previous study by Häkkinen et al. (2012) showed that the MFR
618 (excluding rBC) at 280°C correlated well with anthropogenic tracers (i.e., polycyclic aromatic
619 hydrocarbons), indicating that the non-volatile species may be affected by anthropogenic
620 emissions. In this study, we investigate the sources of the non-volatile organics by comparing the
621 measurements of HR-ToF-AMS and SP-AMS after heating at 250°C. While the HR-ToF-AMS
622 measures the bulk total non-refractory organics, SP-AMS only detects the organics associated with
623 rBC when the SP-AMS is operated with the laser vaporizer only (i.e., no tungsten vaporizer)
624 (Onasch et al., 2012). Figure 11 shows that after heating at 250°C, the residual organics associated
625 with rBC correlate well with the residual organics in the bulk measurements, and they only account
626 for <10% of the bulk measurements. Therefore, this good correlation is not caused by a large
627 contribution from rBC-associated species, but is possibly caused by the fact that the non-volatile
628 organics in the bulk measurements have similar sources or have undergone similar chemical
629 processing as rBC in the atmosphere. Denkenberger et al. (2007) suggested that the non-volatile
630 organics may be oligomers formed within the TD based on the observation that oligomer intensity
631 increased after heating ambient particles in a TD. In our study, the signals at high m/z (100 – 180),
632 which are potential indicators for oligomers, decrease with TD temperature (Fig. S15). This
633 suggests that the non-volatile organics are unlikely to be oligomers formed within the TD.

634 3.3.3 OA MFR and O:C ratio

635 To examine the relationship between O:C and MFR, the O:C of thermally-denuded OA is
636 plotted as a function of TD temperature. As shown in Fig. 12a, the O:C of thermally-denuded OA
637 increases with increasing TD temperature, indicating that the residual OA with lower volatility is
638 more oxidized, which is consistent with previous observations (Huffman et al., 2009a; Huffman et
639 al., 2009b). Thus, it appears that the OA oxidation level (i.e., O:C) is correlated with MFR. If so,
640 one would expect that ambient OA with higher O:C should have larger MFR. However, as shown
641 in Fig. 12b to e, the MFR increases only slightly with the bypass O:C (or OS) over a wide range
642 of O:C (or OS). In addition, the correlation between MFR and bypass O:C (or OS) is weak (i.e., R
643 < 0.4), suggesting that the volatility of OA cannot be readily inferred by its O:C or OS.

644 The lack of correlation between OA MFR and O:C is likely due to the distributions of
645 volatility and O:C in bulk OA, that is, one population of particles with a higher bulk O:C could
646 have lower MFR after heating compared to another population of particles with a lower bulk O:C,
647 if the volatility and O:C distributions are different between two populations. In the following
648 discussion, we use a simple model to illustrate our point (Fig. 13). Two populations of particles
649 are comprised of three compounds (i.e., A, B, and C), but with different amounts. These three
650 compounds have the same molecular weight, but different volatility and O:C. The assumed
651 properties of the three compounds and the compositions of two populations of particles are
652 atmospherically relevant and are summarized in Fig. 13. Although the average O:C of population
653 #2 (i.e., 0.75) is higher than that of population #1 (i.e., 0.61), population #2 has the same MFR as
654 population #1 after heating, which is consistent with the trend in Fig. 12b-e. On the other hand,
655 the O:C of each population always increases after heating, which is consistent with the observation
656 in Fig. 12a. We note that the example described here is specific; however, it clearly illustrates that
657 the distributions of volatility and O:C largely influence the relationship between O:C and MFR of
658 bulk OA. This also helps to explain the various types of relationship between O:C and MFR
659 observed in laboratory studies (Grieshop et al., 2009b; Qi et al., 2010; Donahue et al., 2012; Kroll
660 et al., 2009; Tritscher et al., 2011; Xu et al., 2014). In previous laboratory studies, while the SOA
661 generally becomes progressively more oxidized (i.e., O:C increases) during the chemical aging,
662 the volatility distribution evolves differently for different SOA systems, which results in various
663 types of MFR trend (i.e., increases, or stays constant, or decreases over time). Our analysis

664 emphasizes the importance of understanding the distribution of volatility and O:C in bulk OA and
665 reveals the potential weakness of using one averaged O:C value to describe the degree of oxidation,
666 which is in line with the two-dimensional volatility-oxidation modeling framework proposed by
667 Donahue et al. (2011). In addition to the distribution of O:C and volatility, the fact that MFR
668 depends on the initial concentration of OA, which is different between studies, may also contribute
669 to the various relationships between O:C and MFR.

670 Hildebrandt et al. (2010) proposed that the lack of correlation between O:C and volatility
671 in Finokalia, Greece was caused by the OA being highly oxidized with an average O:C of 0.8
672 (estimated from the measured f_{44}). In order to test this hypothesis, we plot the O:C enhancement
673 (i.e., ratio between O:C of thermally denuded OA and O:C of ambient OA) vs. O:C of ambient
674 OA (Fig. 14a) to show the O:C enhancement after heating. By extrapolating the linear fit under
675 different temperatures, we find that if the O:C of ambient OA is about 1, the enhancement is
676 negligible even after heating at 250°C. It is important to note that the O:C reported in Fig. 14a is
677 calculated based on the recent formulation in Canagaratna et al. (2015). The improved O:C
678 calculation method in Canagaratna et al. (2015) results in higher O:C compared to the values based
679 on Aiken et al. (2008), which was used in Hildebrandt et al. (2010). By using the method in Aiken
680 et al. (2008), we found that the O:C threshold for no enhancement is 0.8 (Fig. S16), which is the
681 same as the O:C of ambient OA in Hildebrandt et al. (2010). In addition, the campaign-average f_{44}
682 of ambient OA in Hildebrandt et al. (2010) is 0.182, which is close to f_{44} of TD OA under 250°C
683 (i.e., 0.188) in our study (Fig. 14b). To conclude, this analysis provides a specific case in which
684 the average O:C ratio might not be a good indicator of OA volatility.

685 **4 Conclusions**

686 In this study, we deployed a suite of instruments to characterize the composition of PM₁ at
687 a rural site (Detling, Kent) near London during the Clean Air for London (ClearLo) project in
688 2012 winter. Nitrate and organics are two major components in PM₁, each of which accounts for
689 ~30% of total PM₁ mass concentration. Retroplume analysis reveals that the PM₁ concentration in
690 the greater London area is largely influenced by the origin of the air masses. When air masses are
691 advected from mainland Europe, the PM₁ concentration is elevated and the organic aerosol is more
692 oxidized. Oxygenated organic aerosol (OOA) accounts for ~50% of total OA. Taking advantage

693 of measurements in winter when the biogenic emissions are low, we hypothesize that the OOA in
694 the current study is likely aged OA from biomass burning. The hypothesis is based on the
695 combined PMF and radiocarbon analysis where more than 70% of carbon in OOA is estimated to
696 be non-fossil (Liu et al., 2015) and cannot be explained by the small amount of biogenic SOA in
697 winter.

698 With simultaneous HR-ToF-AMS measurements taking place at the rural Detling site and
699 the urban North Kensington site, we have a unique opportunity to investigate the spatial variability
700 of PM₁ in the greater London area. The nitrate concentration is markedly higher at the urban site
701 compared to the rural site (i.e., 5.6 vs 3.5 $\mu\text{g m}^{-3}$). The high nitrate concentration at the rural site
702 together with the urban excess of nitrate imply that the nitrate in the greater London area has a
703 high regional background overlaid by important contributions from local production. Although the
704 OA concentration is comparable between the rural and urban sites, PMF analysis suggests
705 distinctly different contribution from different sources between the two sites. Similar to previous
706 studies, we find that OA at the urban site mainly arises from primary sources, while OA at the
707 rural site is mainly secondary. Vehicle emission, solid fuel combustion, and cooking together
708 account for $\sim 70\%$ of OA at the urban NK site. In contrast, OOA contributes more than half of total
709 OA at the rural Detling site. Among all OA factors, OOA has the best correlation between the two
710 sites ($R = 0.81$), which suggests that this factor is largely regional. We find that the OOA
711 concentration is almost twice as high at the rural Detling site than the urban NK site. This is a
712 result of meteorological conditions, which cause a strong gradient of SOA concentration when air
713 masses are advected from polluted mainland Europe. The observation that the OOA concentration
714 is higher at the rural site than urban site is opposite to the trend shown in Zhang et al. (2007).
715 However, the trend reported in Zhang et al. (2007) is not based on simultaneous measurements at
716 paired rural and urban sites. Thus, our observation highlights the importance of meteorology in
717 determining the OA spatial distribution.

718 A TD was deployed to investigate the volatility of PM₁ species at the Detling site. We find
719 that although OOA has substantial larger O:C than HOA and SFOA, the volatilities of these three
720 factors are similar at 120°C, which is inferred from the change in mass concentration after heating
721 at 120°C. This suggests that the O:C may not be a good proxy of OA factor volatility. We note
722 that 16% of total OA remains even after heating at 250°C, suggesting the existence of non-volatile

723 organics. PMF analysis reveals that the majority of the remaining organics are oxygenated OA. At
724 250°C, the time series of the residual organics measured by HR-ToF-AMS correlate well with the
725 residual organics associated with rBC measured by SP-AMS. The good correlation suggests that
726 the non-volatile organics likely have similar sources or have undergone similar chemical
727 processing as rBC in the atmosphere, considering that rBC-associated organics only account for
728 <10% of bulk organics.

729 We evaluate the relationship between the volatility (using the MFR) and degree of
730 oxidation (using the O:C or OS) of bulk OA. We found that, on the one hand, the O:C of thermally
731 denuded OA is higher than that of ambient OA, indicating that less-volatile compounds have
732 higher O:C. On the other hand, the MFR of OA shows a weak correlation with O:C of ambient
733 OA, indicating that the average O:C of bulk OA may not be a good indicator for volatility. One
734 possible explanation for the seemingly contradictory observations lies in the broad distribution of
735 volatility and O:C in bulk OA. For example, different O:C distributions could result in the same
736 bulk O:C but different volatility distributions, which may cause that particles with the same O:C
737 to have different MFR. Thus, it is important to understand and use the distribution of properties
738 (i.e., volatility and O:C) to describe the complexity of OA.

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1266 **Figure Captions**

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1268 Fig. 1. Geographical locations of the sampling sites (i.e., North Kensington and Detling) in this
1269 study. The region circled by the M25 motorway is the greater London area. The map is adapted
1270 from Google Maps.

1271 Fig. 2. Scatter plot of converted volume (based on HR-ToF-AMS total + BC + crustal material)
1272 vs. the apparent volume estimated from SMPS measurement for (a) the bypass line and the TD
1273 line at (b) 120°C and (c) 250°C. The composition-dependent CE is applied to the bypass line HR-
1274 ToF-AMS measurements and CE = 0.45 is applied to the TD line HR-ToF-AMS measurements.
1275 The slopes and intercepts are obtained by orthogonal distance regression (ODR). The Pearson's R
1276 is obtained by linear least-squares fit.

1277 Fig. 3. (a) Time series of non-refractory species and black carbon in addition to the flag waves of
1278 dominant air mass origin based on the NAME model. (b) Average concentration of non-refractory
1279 species, black carbon, and OA factors resolved by PMF analysis for the easterly sector, westerly
1280 sector, and the whole campaign. The unexplained mass by PMF analysis is less than 6% of total
1281 OA and not shown in the figure. The gap between 1/22 and 1/25 is due to a clogged instrument
1282 inlet.

1283 Fig. 4. (a) Time series of OA factors resolved from the unconstrained PMF analysis on the ambient
1284 data (i.e. PMF_{ambient}) and corresponding external tracers. (b) Mass spectra of OA factors, which
1285 are colored by the ion type. The time series of total nitrated phenols is from Mohr et al. (2013).

1286 Fig. 5. f_{44} vs. f_{43} for Detling and NK sites, as well as for the westerly sector and easterly sector of
1287 the Detling site. The dotted lines were adapted from Ng et al. (2010). The averages are sized by
1288 average organic loading. The error bars indicate one standard deviation. The average OA
1289 concentration at the Detling site is different from the value in Fig. 3 due to different sampling
1290 periods.

1291 Fig. 6. Comparison between NK and Detling sites in terms of the campaign-averaged concentration
1292 and mass fraction of non-refractory species and OA factors. The unexplained mass by PMF
1293 analysis is less than 6% of total OA and not shown in the figure.

1294 Fig. 7. Comparison of non-refractory species time series between NK and Detling sites. The
1295 intercept and slope are obtained by orthogonal distance regression. The Pearson's R is obtained by
1296 linear least-squares fit.

1297 Fig. 8. Comparison of OA factors time series between NK and Detling sites. The intercept and
1298 slope are obtained by orthogonal distance regression. The Pearson's R is obtained by linear least-
1299 squares fit.

1300 Fig. 9. Thermogram of (a) non-refractory species and (b) OA factors. The change in mass
1301 concentration after heating in the TD (i.e., ΔC) of (c) non-refractory species and (d) OA factors.

1302 Error bars indicate one standard deviation. The average values are connected by lines to guide the
1303 eyes.

1304 Fig. 10. Mass fraction of PM₁ species for bypass line and TD line (i.e., 120°C and 250°C). The
1305 mass fractions larger than 9% are labeled in the figure.

1306 Fig. 11. Comparison between organics associated with rBC (measured by SP-AMS with laser
1307 vaporizer only) and the non-refractory organics in the bulk measurement (by HR-ToF-AMS) after
1308 heating at 250°C.

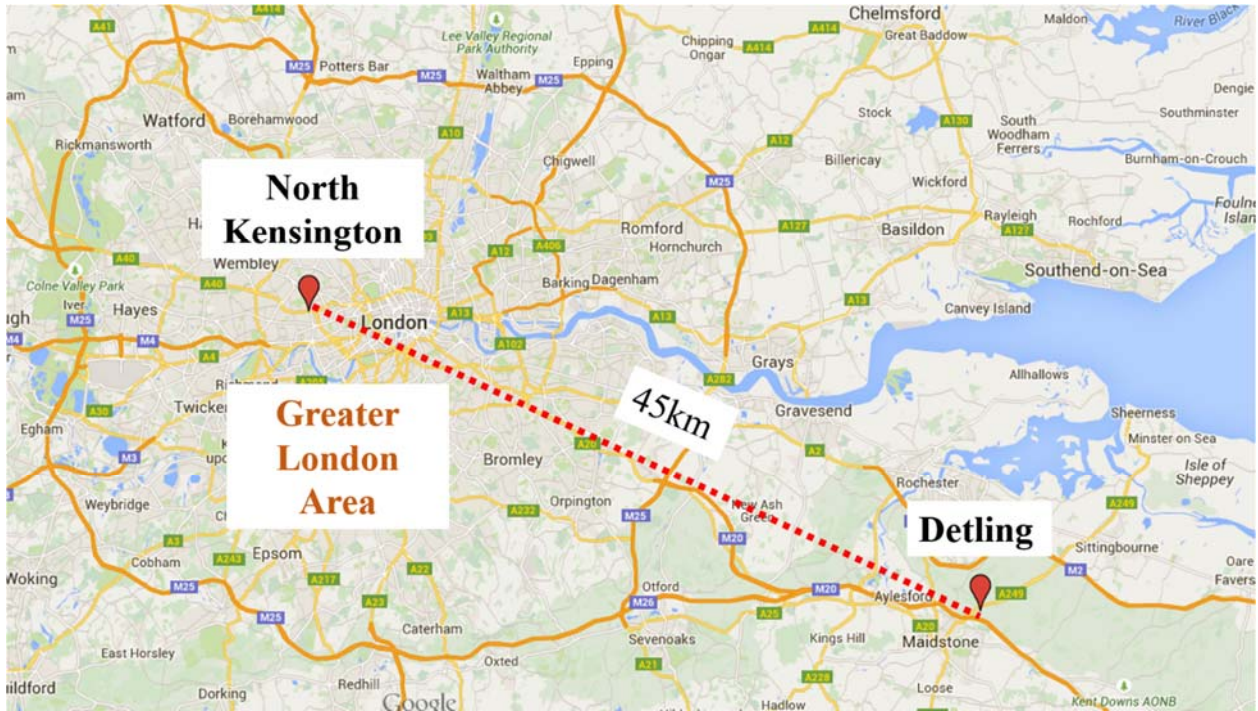
1309 Fig. 12. (a) Organic mass fraction remaining (MFR) and O:C as a function of TD temperature; (b)
1310 – (e) organic MFR at 120°C and 250°C as a function of bypass line organic O:C and oxidation
1311 state.

1312 Fig. 13. The properties (O:C and volatility) of three model compounds and the composition of two
1313 populations of particles used in the simple model to illustrate the relationship between bulk OA
1314 O:C and volatility. The O:C is 1, 0.5, and 0.1 for compound A, B, and C, respectively. Upon
1315 heating at temperature T₀, 50%, 65% and 100% of A, B, and C would evaporate. Population #1 is
1316 comprised of 0.25, 0.7, and 0.05 μg m⁻³ of A, B, and C, respectively, and population #2 is
1317 comprised of 0.7, 0.05, and 0.25 μg m⁻³ of A, B, and C, respectively.

1318 Fig. 14. (a) O:C enhancement (i.e., ratio of TD line O:C to bypass line O:C) as a function of bypass
1319 line O:C. (b) Mass spectra of OA under different TD temperatures. The signals between *m/z* 45
1320 and 99 are multiplied by 10 and the signals between *m/z* 100 and 150 are multiplied by 25 for
1321 clarity. The mass spectra are colored by the ion type in the same way as Fig. 4b.

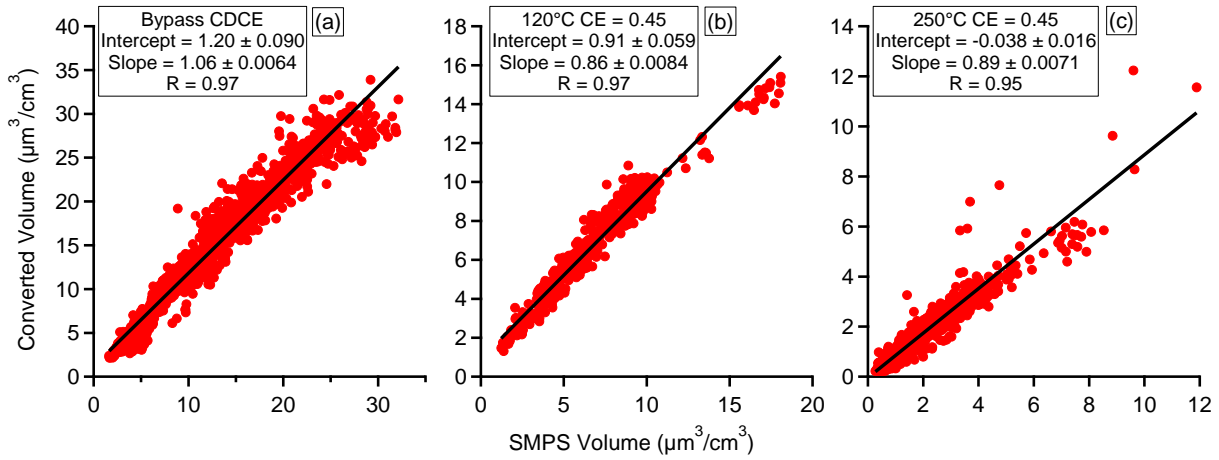
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1340 Fig. 1



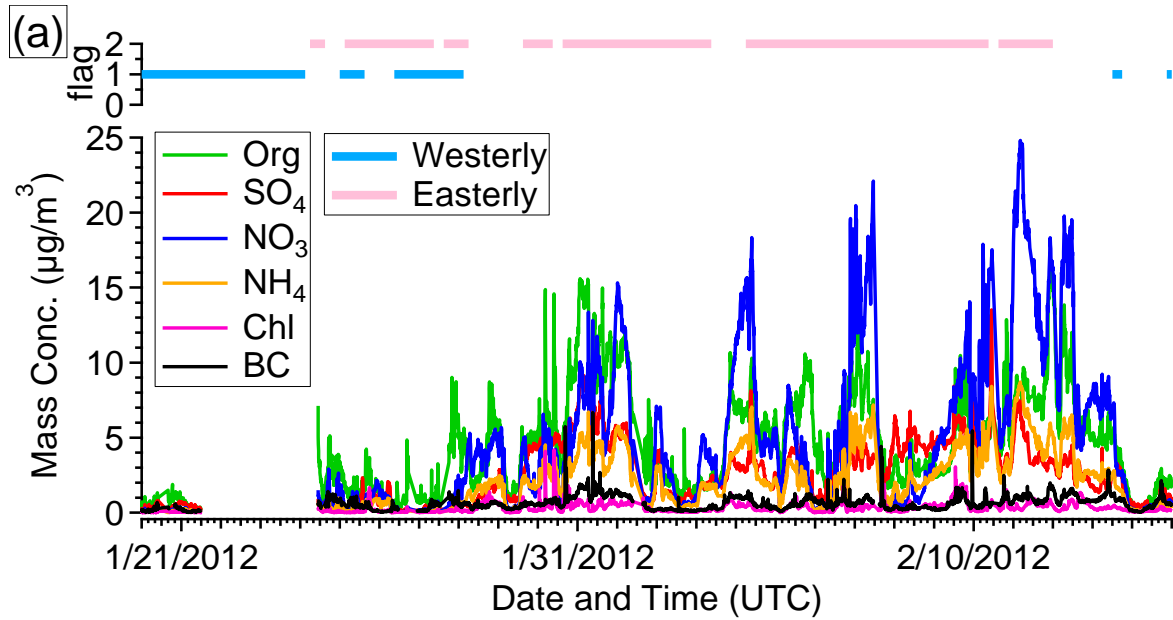
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1365 Fig. 2

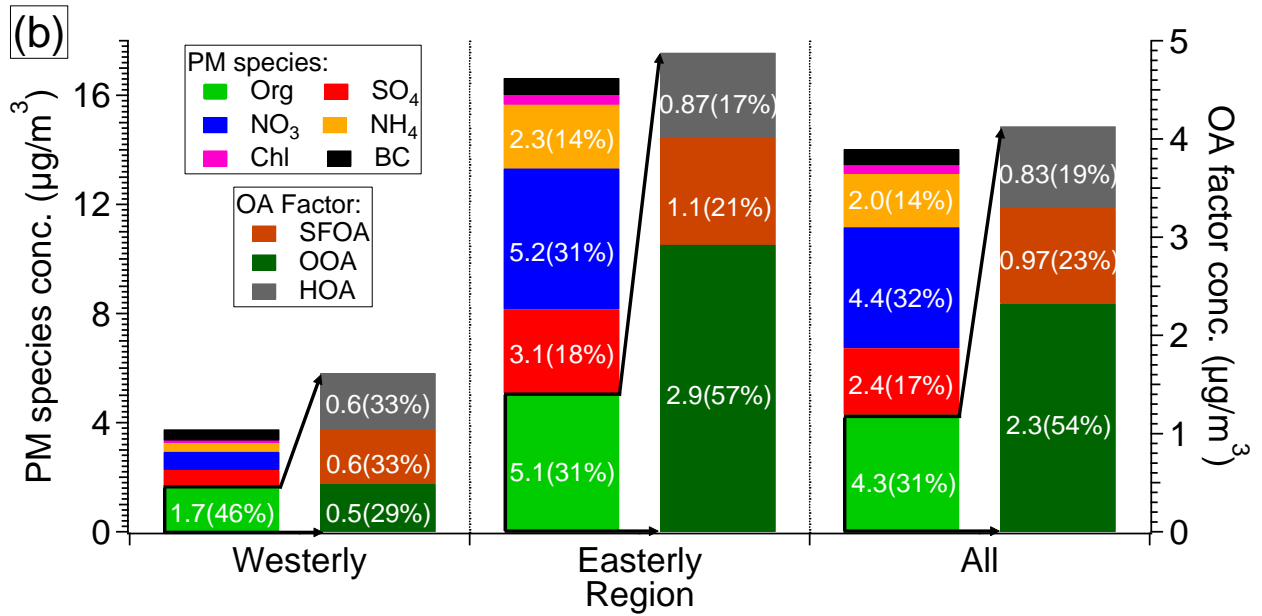


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1396 Fig. 3

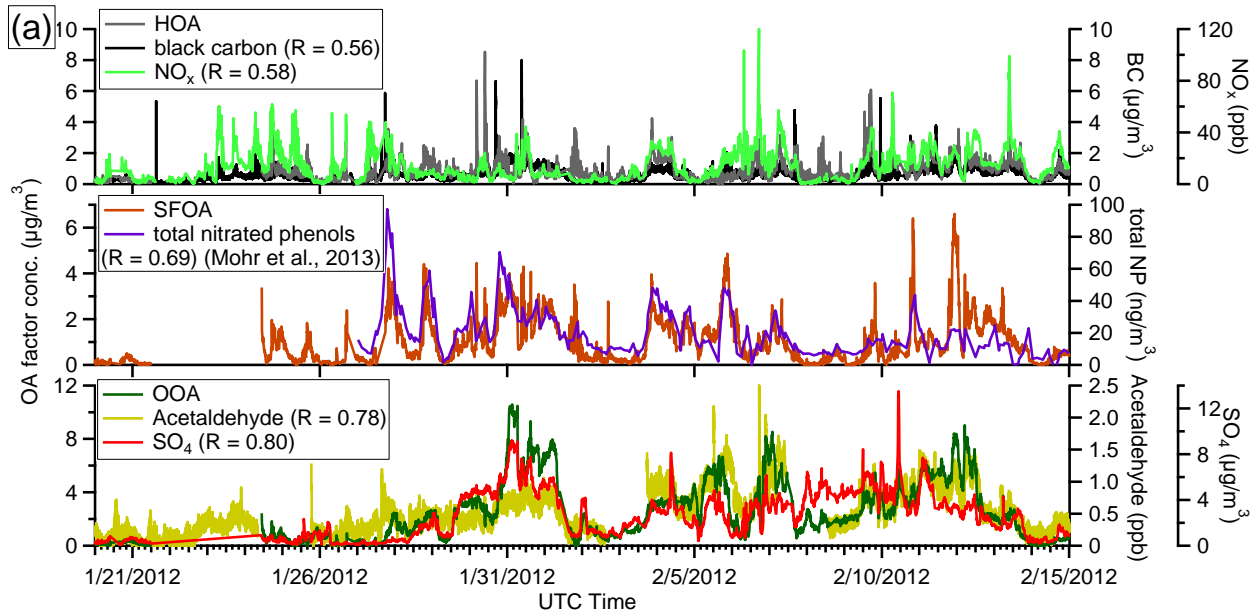


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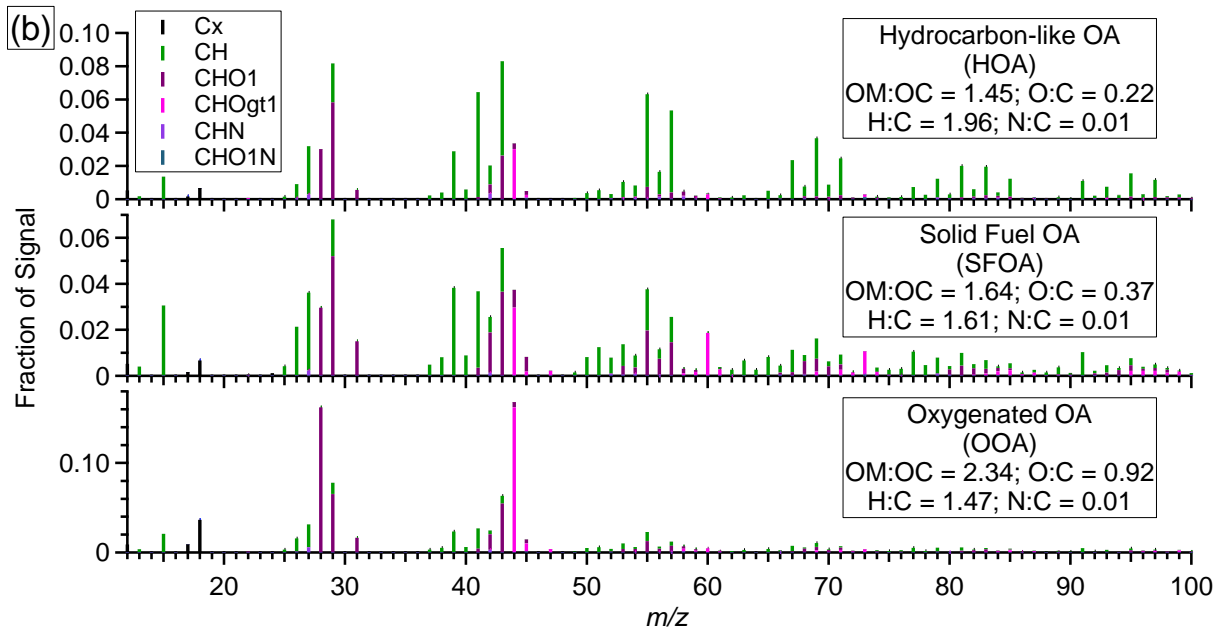


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1409 Fig. 4



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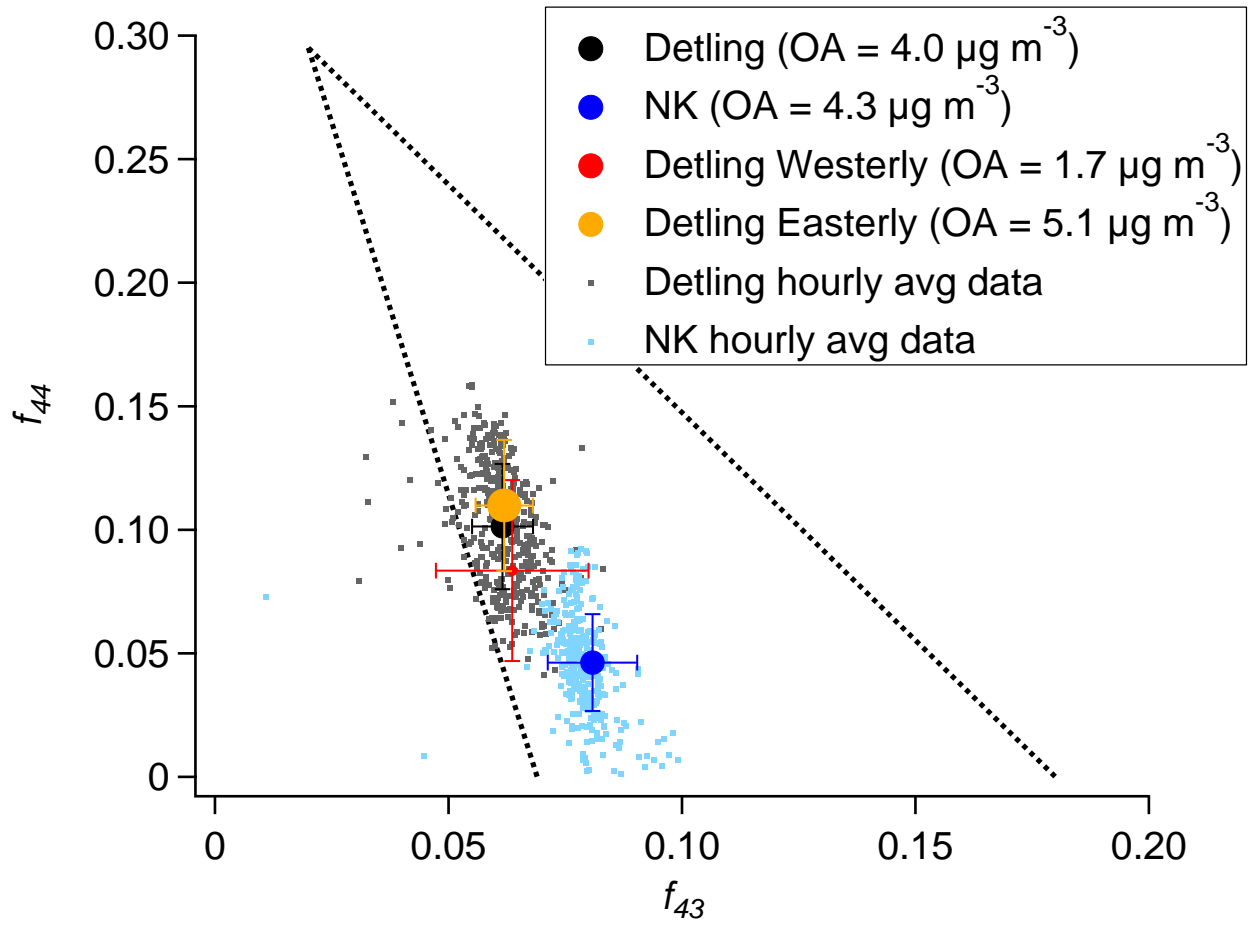
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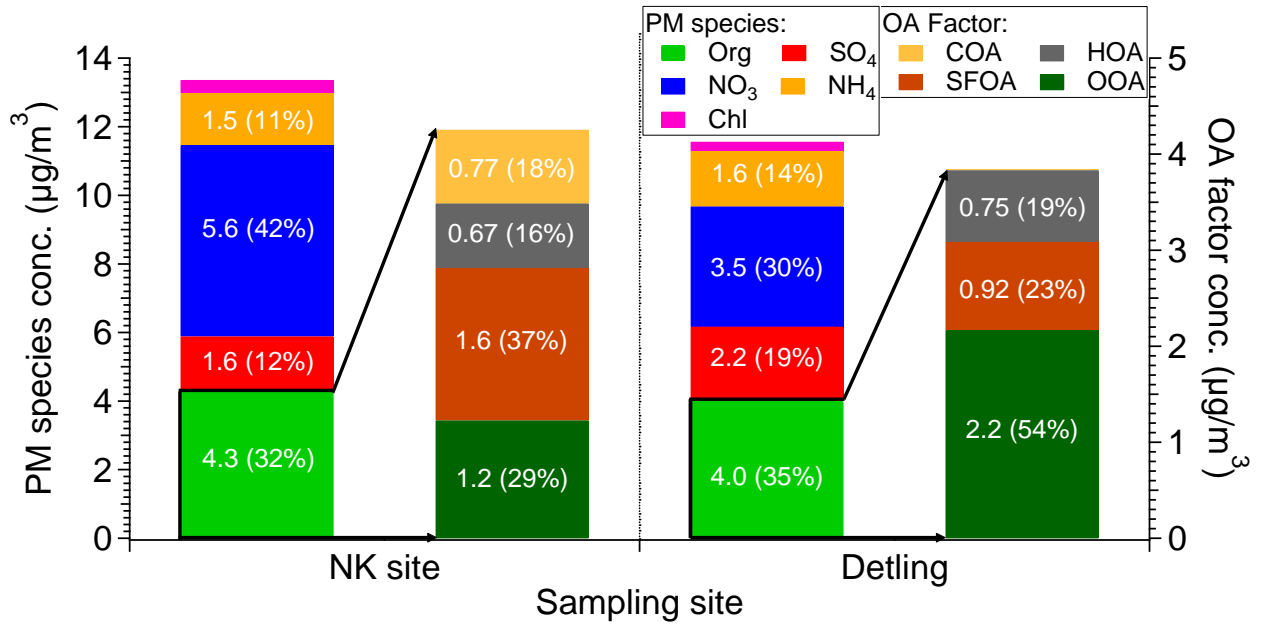
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1422 Fig. 5



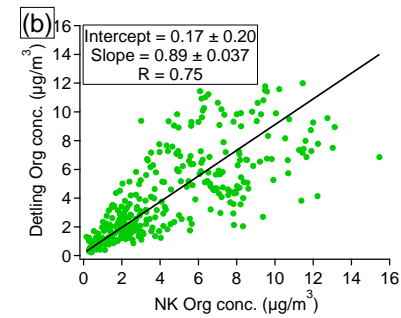
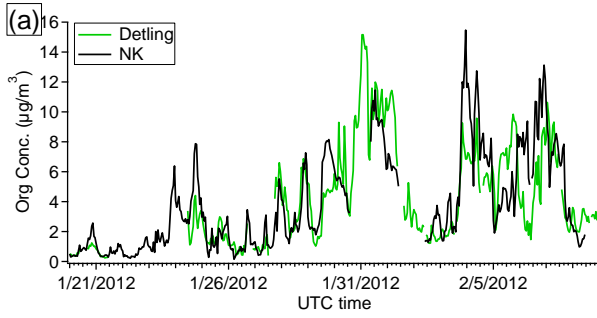
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1441 Fig. 6

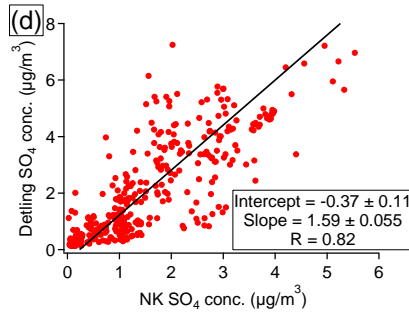
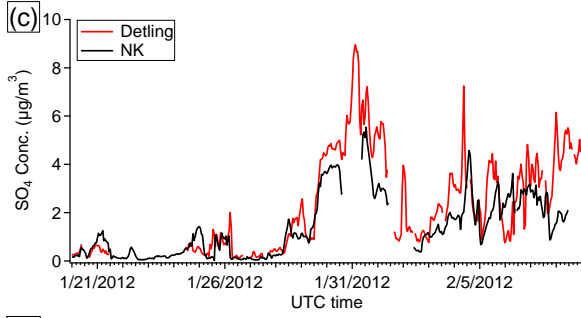


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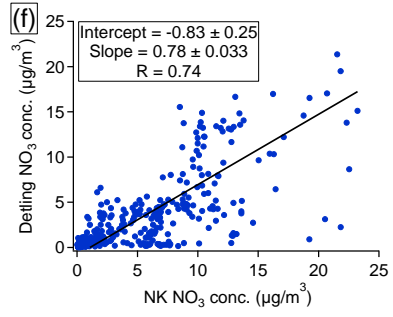
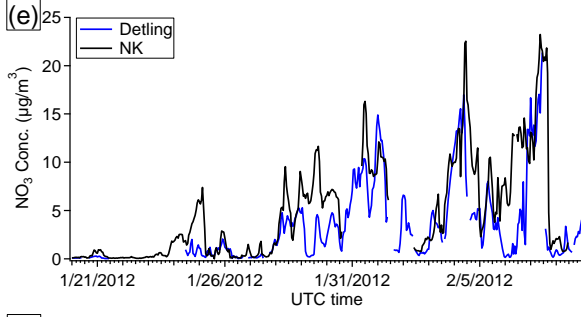
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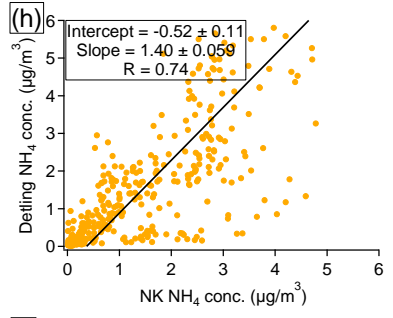
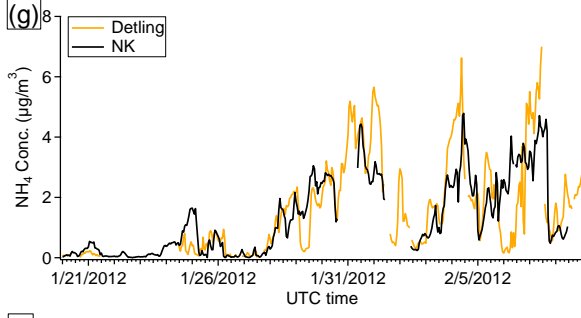
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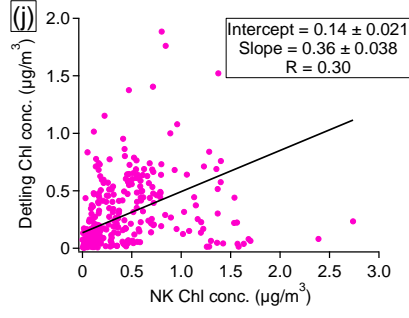
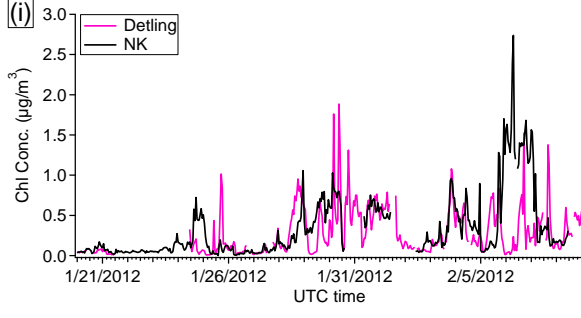
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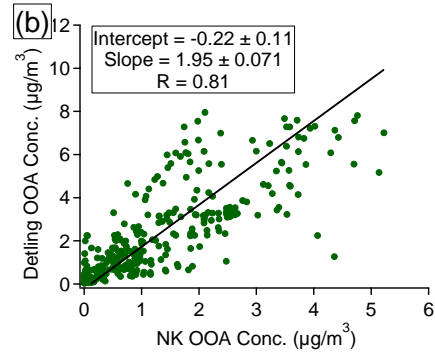
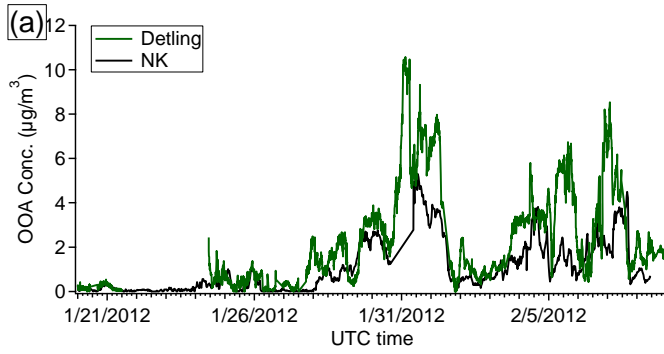


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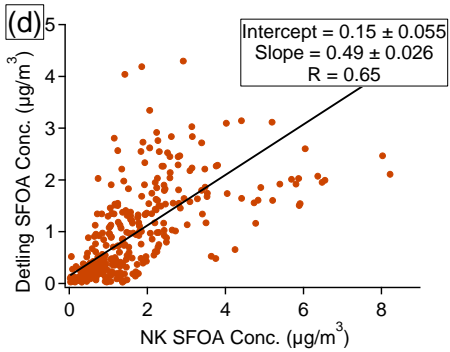
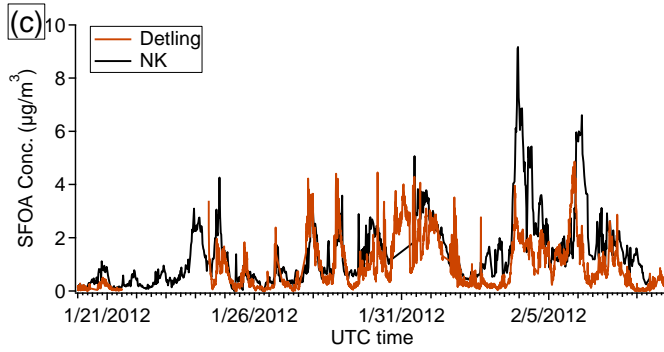


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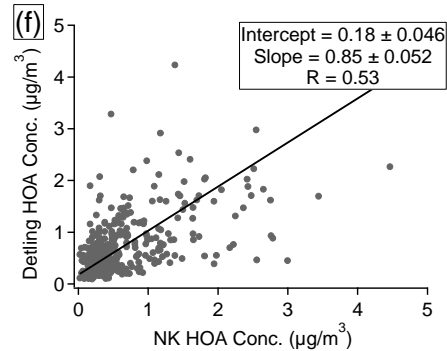
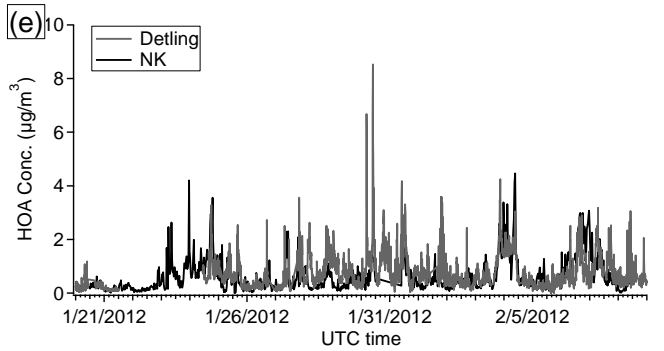
1474 Fig. 8



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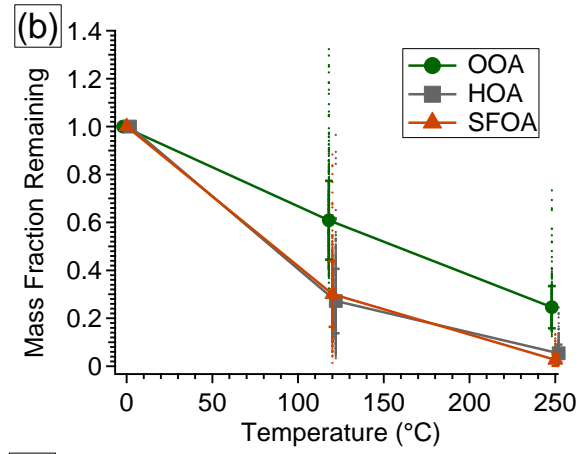
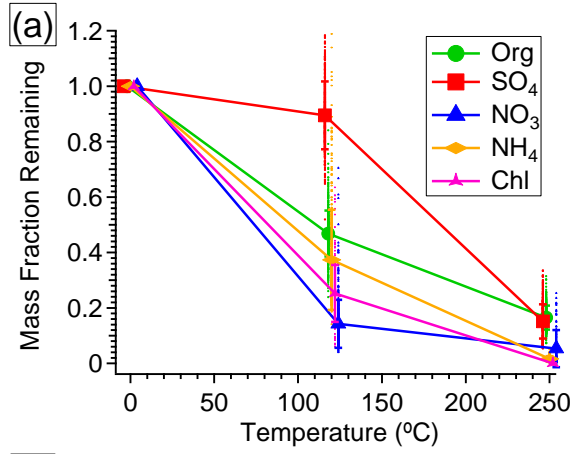
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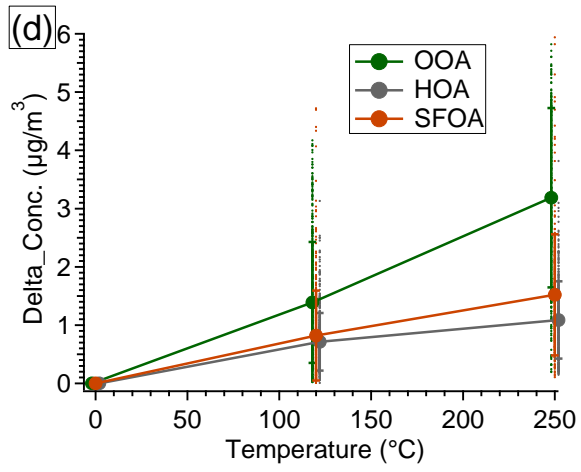
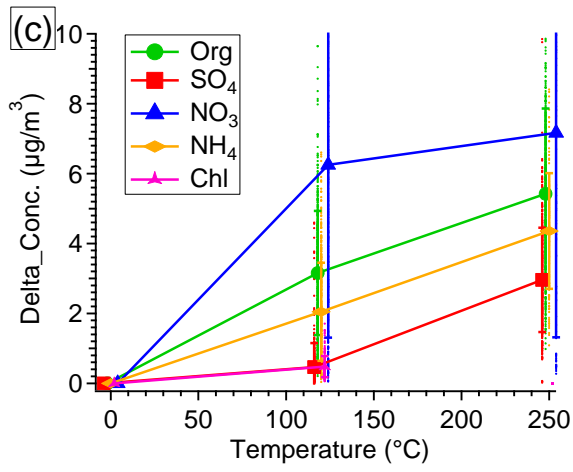
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1485 Fig. 9



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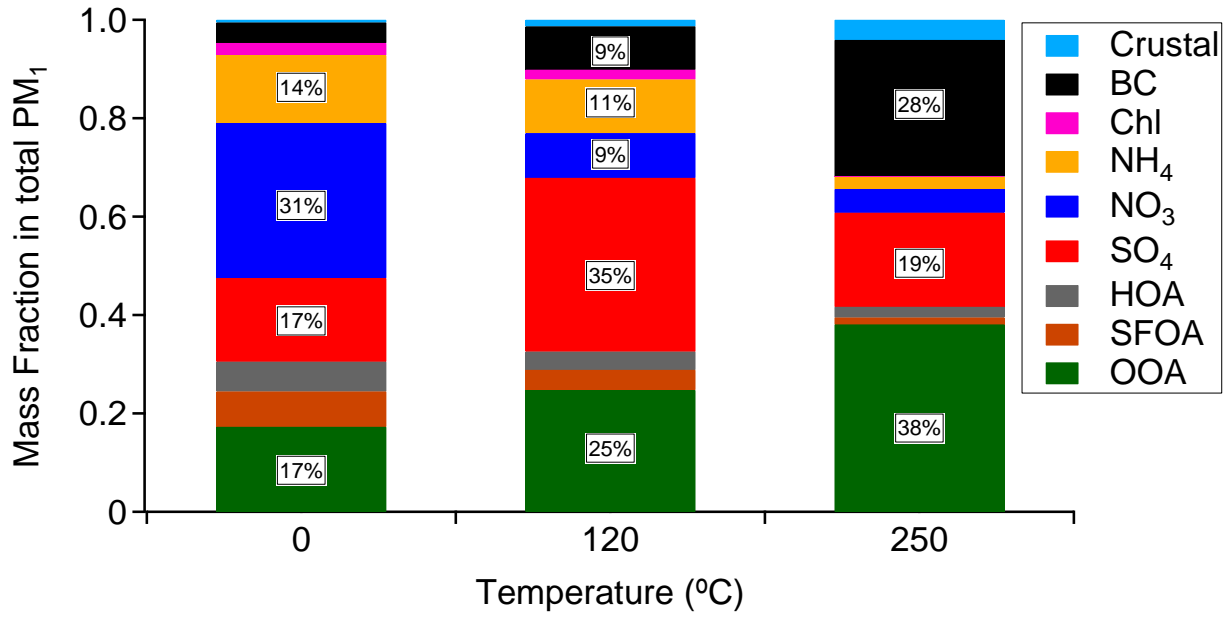
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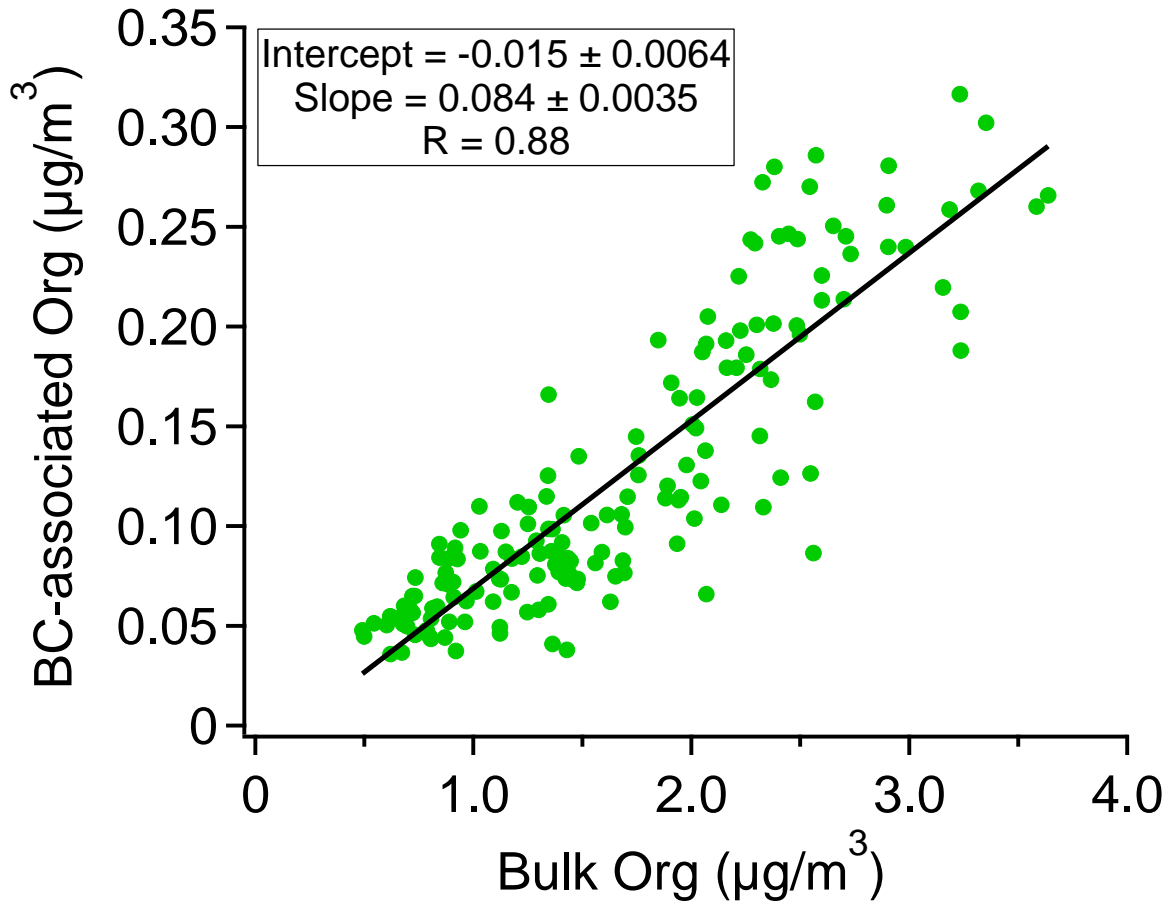
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1506 Fig. 10



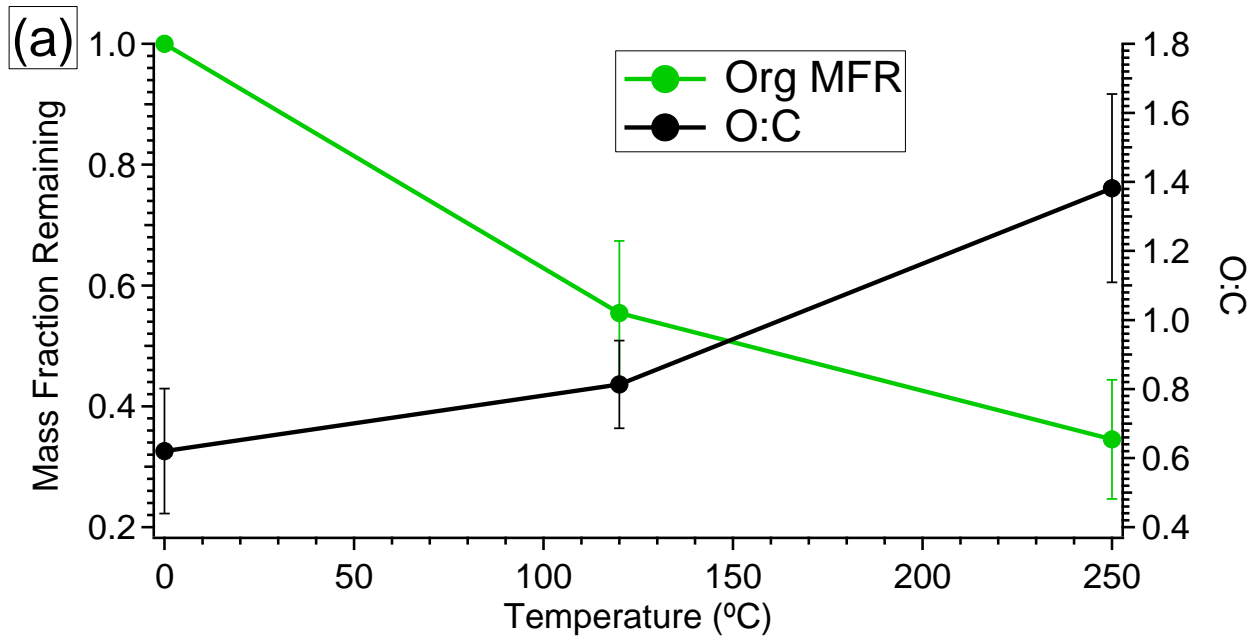
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1532 Fig. 11

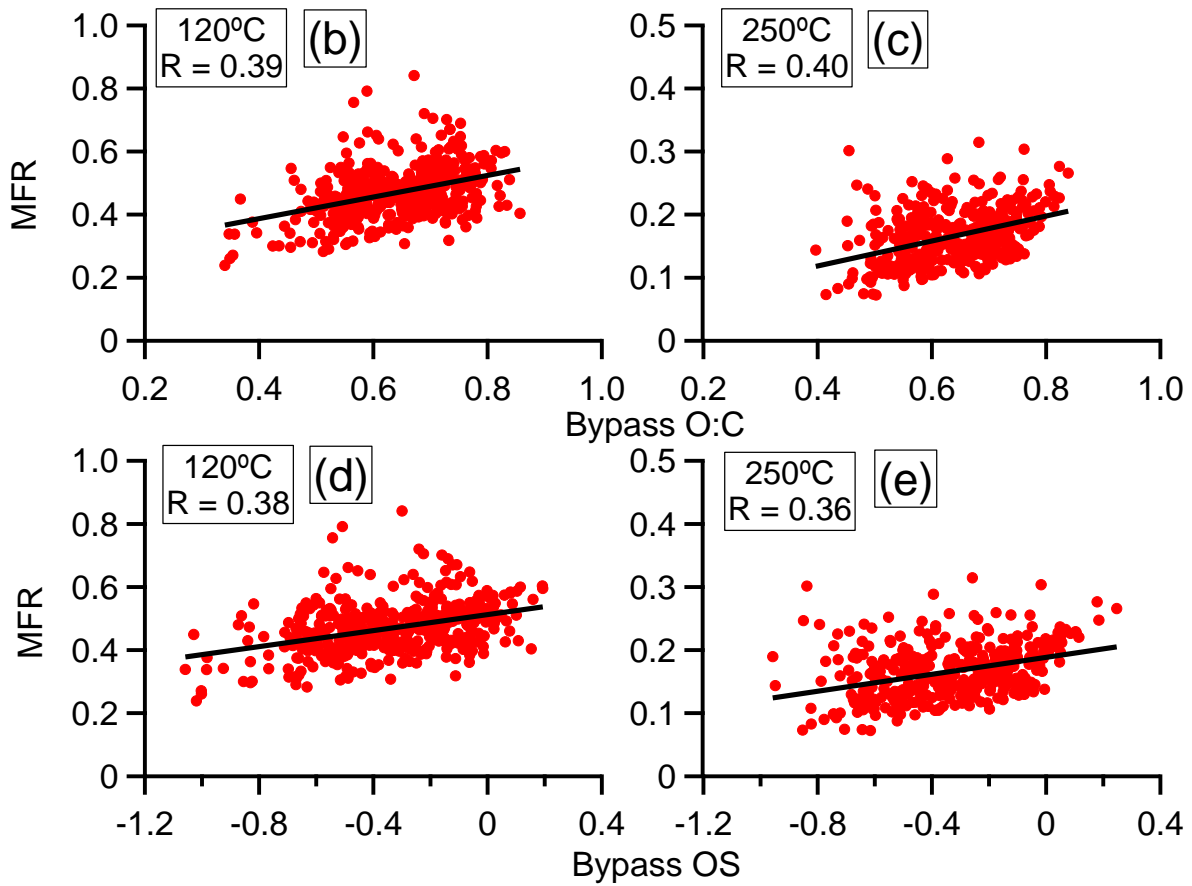


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1551 Fig. 12



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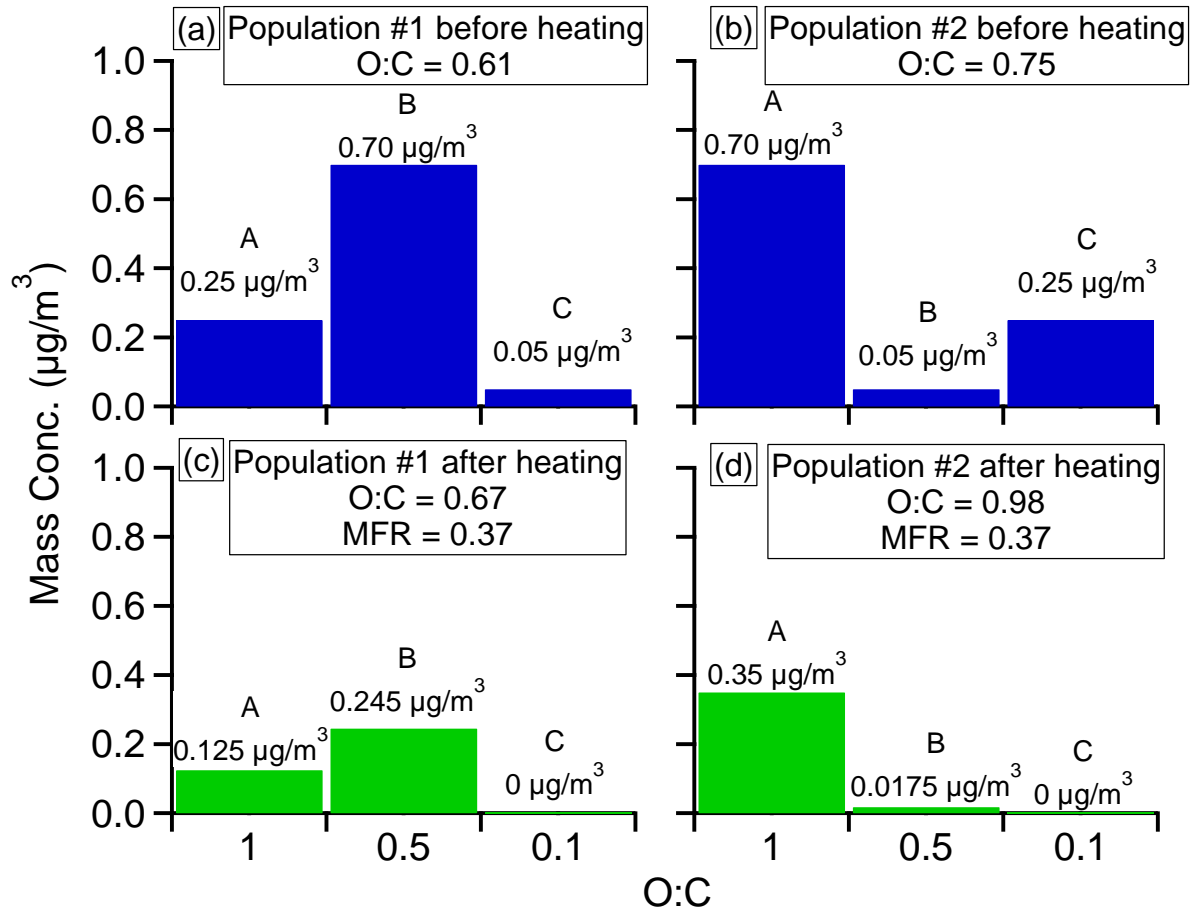
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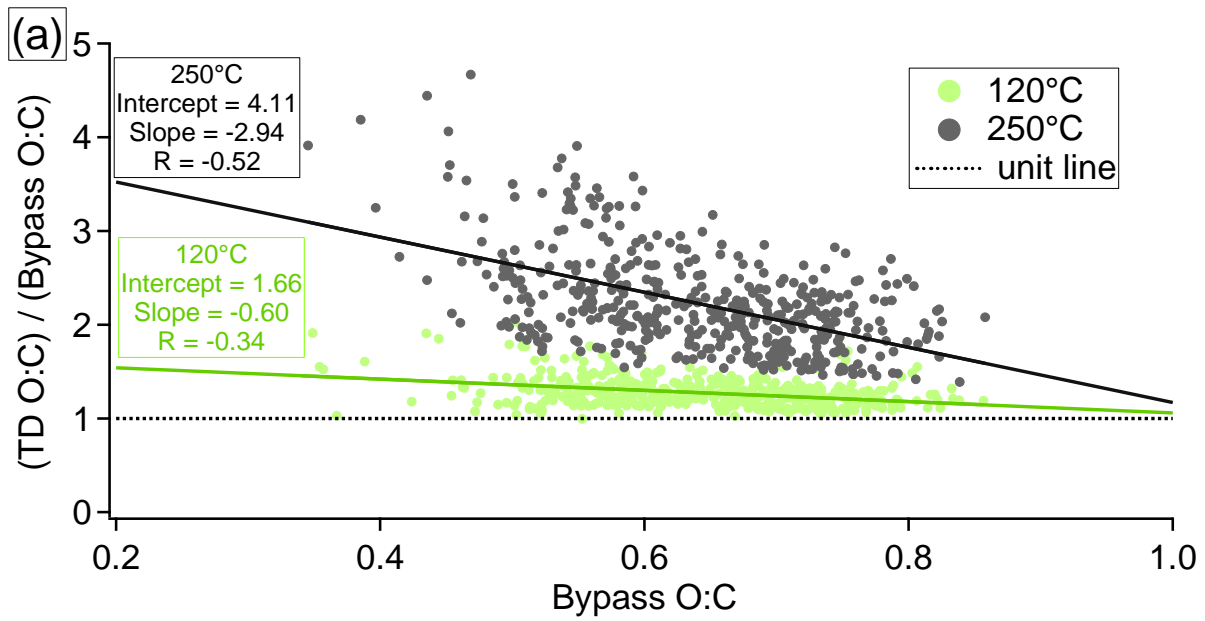
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1557 Fig. 13

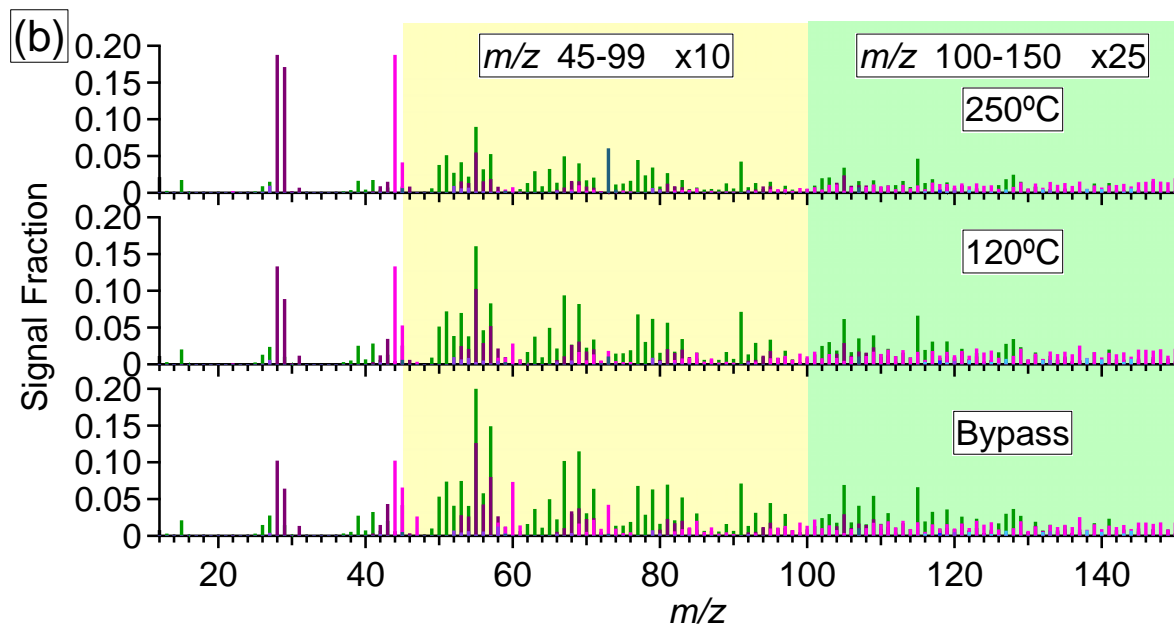


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1576 Fig. 14



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