



Supplement of

Influence of anthropogenic emissions on the composition of highly oxygenated organic molecules in Helsinki: a street canyon and urban background station comparison

Magdalena Okuljar et al.

Correspondence to: Magdalena Okuljar (magdalena.okuljar@helsinki.fi)

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13 **S1. Overview of meteorological variables and trace gases measurements**

14 Table S1. Overview of additional variables measured at the urban background and the street canyon sites.

Variable [unit]	Instrument / model	Height of measurement (m)
Urban background station		
NO, NO_x [ppb]	chemiluminescence analyzer / Horiba APNA 370	4
O₃	UV-absorption / Teledyne Instruments API 400E	4
SO₂ [ppb]	UV fluorescence analyzer / Thermo Fisher Scientific TEI 43iTLE	4
Relative humidity [%]	Vaisala HMP243	29
Air temperature [°C]	Pentronic Pt100	4
Wind direction [°]	2D ultrasonic anemometer/ Thies Clima 2.1x	32
Wind speed [m/s]	2D ultrasonic anemometer/ Thies Clima 2.1x	32
Global radiation [W/m²]	Kipp and Zonen CNR1	32
Black carbon	Multi Angle Absorption Photometer (MAAP), Thermo Scientific, Model 5012	4
Street canyon		
NO, NO_x [µg/m³]	chemiluminescence analyzer / Horiba APNA 370	4
O₃ [µg/m³]	UV fluorescence analyzer / Horiba APOA-370	4
Relative humidity [%]	Vaisala WXT 536	4
Air temperature [°C]	Vaisala WXT 536	4
Wind speed [m/s]	Vaisala WXT 536	4
Black carbon	Optical analyzer / MAAP 5012	4

15

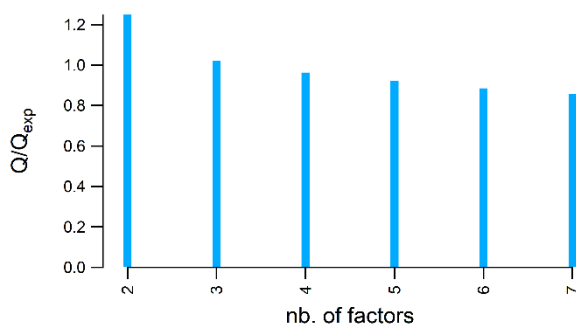
16 S2. PMF inputs and validation

17 Data preparation

18 PMF analysis was performed on three different m/Q ranges from UMR data at each station: 200-350 Th, 350-500 Th, and
19 500-650 Th (range 1, 2, and 3). The time resolution of the input data was 30 minutes. At the urban background station,
20 during most of the studied time, we detected water clusters; the impurities formed by clustering water molecules with
21 reagent ions. Their appearance in the ambient sample depends on the settings of CI-API-TOF and the sampled RH. For
22 range 1, water clusters were a weighty fraction of the spectrum, thus they were taken out from the data set before running
23 PMF. We removed data at $188 + n*18$ and $251 + n*18$ Th which correspond to $(\text{HNO}_3)_{2-3}(\text{H}_2\text{O})_n\text{NO}_3^-$ molecules.
24 Additionally, the reagent ion tetramer $(\text{HNO}_3)_3\text{NO}_3^-$ (251 Th) had a big contribution in the dataset at the urban background
25 site, thus it was removed from the PMF analysis. At the street canyon water clusters and $(\text{HNO}_3)_3\text{NO}_3^-$ were not detected.

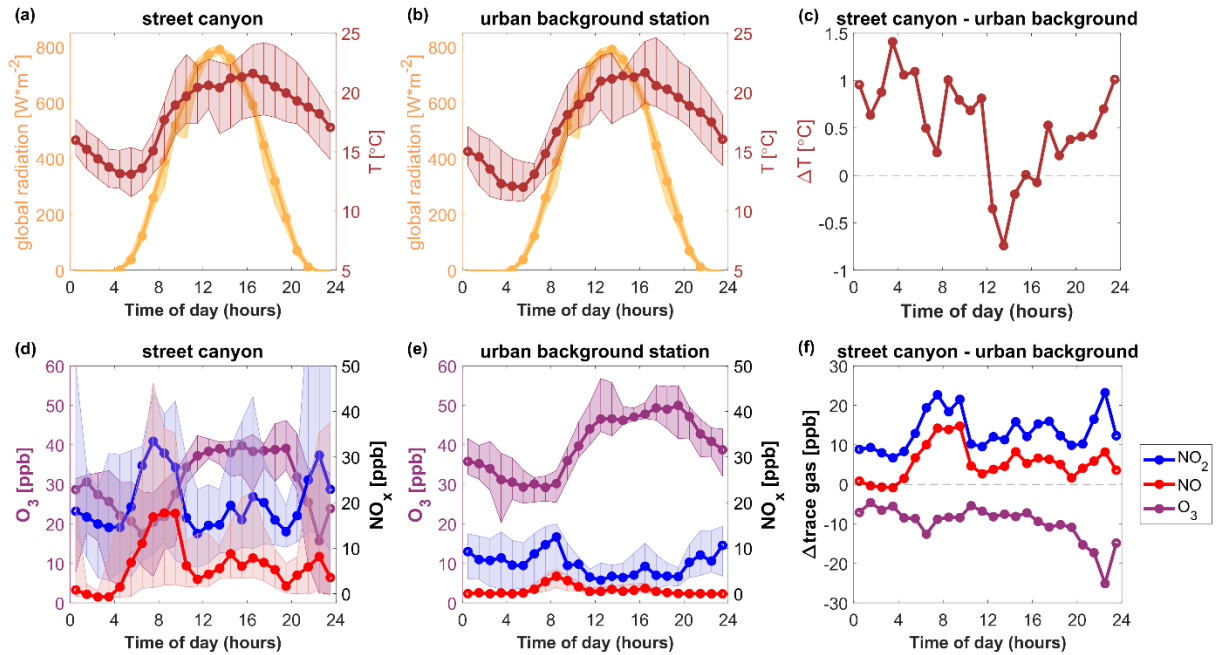
26 Selecting number of factors

27 We performed PMF analysis for a 2-7 factor solution for each range at both stations. For each solution, we analyzed a
28 diagnostic parameter Q/Q_{exp} (Canonaco et al., 2013), which for an ideal PMF run without downweighing would decrease
29 to 1. Since we downweighed errors, we do not expect Q/Q_{exp} to equal 1 but rather stabilize. In all cases we observed
30 stabilization of Q/Q_{exp} value; however, this parameter itself was usually not conclusive enough to determine the number
31 of solutions. Only for range 3 at the street canyon we chose a number of factors primarily based on Q/Q_{exp} (Fig. S1). For
32 that range, 3-factor solution gives Q/Q_{exp} value closest to 1. We chose 3 factors solution also for range 3 at the urban
33 background station. Factor UB3-3 is the only daytime factor in this range and including it in the solution, clarified results
34 of factors 1 and 2. At the same time including more factors did not bring any new information to the solution. For the rest
35 of the PMF solutions at both sites, we chose a 5- or 6-factor solution. We used time series, diurnal variations, and mass
36 spectral profiles to estimate the relevance of different factor solutions for our study. We looked for spectral features or
37 time behaviors that we could associate with atmospheric processes. Alternatively, we included an additional factor if its
38 characteristics differed from all proceeding factors in that solution. In all cases, the unexplained fraction of the spectrum
39 for chosen solution stays between 9 and 12.1%.



40
41 Figure S1. Q/Q_{exp} value for 2-7 factors solution for range 3 at street canyon site.

42 **S3. Overview of meteorological and trace gas conditions for overlapping time of measurements**



43

44 Figure S2. Diurnal variations of (a,b) global radiation and ambient temperature, and (c,d) NO, NO₂, and O₃ concentrations
 45 at the street canyon (left) and urban background station (middle) for the overlapping time of measurements (11 May 2018
 46 13:00:00 – 23 May 2018 15:30:00). The right panel represent the difference between (c) ambient temperature and solar
 47 radiation as well as (f) NO, NO₂, and O₃ concentrations measured at the street canyon and the urban background station.
 48 Presented data contain both workdays and weekends. The median diurnal variations are shown as solid lines with markers;
 49 25th to 75th percentile ranges are presented as shaded areas. Time is local.

50 S4. Factor interpretation

51 In this section, we describe PMF factors and the reasons behind the suggested VOC types, oxidants, terminators, and
52 inhibitors in Tables 1 and S3. As mentioned in section 1, O₃ and NO₃ are selective towards compounds that they react
53 with in the atmosphere, while OH reacts with almost any compound. The chemoselectivity of NO₃ and O₃ towards VOC
54 results in a mass spectrum with a clear pattern, observed before in laboratory experiments (e.g., Ehn et al., 2014; Dam et
55 al., 2022) and ambient measurements (e.g., Yan et al., 2016). At the same time, a mass spectra containing HOM oxidized
56 by OH looks messier, as OH oxidized most VOC in the atmosphere. In the description of factors, we say that we observe
57 chemoselectivity of the oxidant when we notice a pattern in the mass spectrum, and we call the oxidant not chemoselective
58 when there is no pattern in the mass spectrum. We are not able to analyze the influence of HO₂ as a terminator, thus HO₂
59 could potentially be a terminator for all the factors, except for factors UB3-2 and SC3-1, which must be terminated by
60 RO₂. All key compounds were detected as clusters with NO₃⁻, however, for clarity of the interpretation we write their
61 chemical structures in the descriptions without the NO₃⁻ adduct.

62 • Street canyon

63 • Selected factors

64 All factors from range one at street canyon are marked as ‘not selected’, thus the description of selected factors at street
65 canyon starts with range 2. The timeseries of the SC factors are shown in Figure S3, diurnal variation at Figure 3 in main
66 text, and spectra are presented in Figure S5.

67 SC2-1, "MT monomers 1"

68 **Temporal behavior:** SC2-1 factor is a daytime factor reaching maximum concentration at 13:00, suggesting that either
69 OH or O₃ is the main oxidant.

70 **Spectral features:** The key compounds contain C₁₀H₁₆O₈₋₉N₂, and possible: C₁₀H₁₆O₉₋₁₀N, C₁₀H₁₆O₁₀, C₉H_{14,16}O₉N₂, and
71 C₉H₁₄O₁₀N₂ (Table S2) suggesting biogenic origin of this factor: MT. The pattern in mass spectrum suggests
72 chemoselectivity of the oxidant towards VOC precursors (Fig. S5), which could imply that the main oxidant is O₃, even
73 though OH could also participate in oxidation reactions. The presence of ONCs suggests that NO is the main terminator.

74 **Other:** SC2-1 correlates with *SC1-1: nitrophenol 1* (R=0.87), *SC1-5: nitrophenol & aliphatic* (R=0.78), *SC3-2:*
75 *photooxidation* (R=0.88) as well as *UB1-2: nitrophenol* (R=0.75), and *UB1-6: C7-8* (R=0.66).

76 SC2-2, "370+433"

77 **Temporal behavior:** SC2-2 reaches the highest concentrations during nighttime at 11 p.m., but it is also present during
78 the morning. Diurnal variation suggests NO₃ or O₃ as oxidants.

79 **Spectral features:** SC2-2 is a factor mostly driven by one compound: C₁₀H₁₆O₉N₂ (Table S2), which is detected as two
80 separate clusters (370 Th with NO₃⁻ and 433 Th with HNO₃NO₃⁻).

81 **Other:** SC2-2 correlates with *SC1-4: unidentified 2* (R=0.75), *UB2-4: MT monomers 3* (R=0.75) as well as CO₂ (R=0.60)
82 and NO₂ (R=0.58). SC2-2 and *B2-4: MT monomers 3* are both factors driven mostly by C₁₀H₁₆O₉N₂, however, *UB2-4:*
83 *MT monomers 3* contains also other compounds.

84 SC2-3, "MT monomers 2"

85 **Temporal behavior:** SC2-3 reaches the highest concentrations during nighttime, but it is also slightly elevated between
86 11:00 and 16:00. Nighttime behavior suggests that NO₃ is the main oxidant. A morning drop of SC2-3 corresponds to an
87 increase in NO; this indicates that NO may act as an inhibitor for the formation of this factor.

88 **Spectral features:** The key compounds contain C₁₀H₁₆O₁₀₋₁₁N and C₁₀H₁₆O₁₀, which suggests a biogenic origin: MT. The
89 presence of ONCs confirms that NO₃ may be the main oxidant.

90 **Other:** SC2-3 correlates with SC3-1: MT dimers (R=0.72) and UB3-2: MT dimers (R=0.63), both are factors containing
91 MT dimers. This suggests that SC2-3 could be also terminated by RO₂.

92 SC3-1, "MT dimers"

93 **Temporal behavior:** SC3-1 is a nighttime factor with a maximum at 23:00. Since SC3-1 is a nighttime factor, OH does
94 not participate in the oxidation reactions. The diurnal variation suggests that NO is not involved in the termination of this
95 factor, and it acts as an inhibitor.

96 **Spectral features:** SC3-1 contains C₂₀H₃₂O₁₁₋₁₅N₂ (Table S2), which are MT dimers. This implies that RO₂ terminates
97 the formation of SC3-1. The presence of ONCs suggests that NO₃ is the dominant oxidant for this factor.

98 **Other:** SC3-1 correlates with SC2-3: MT monomers 2 (R=0.70) and UB3-2: MT dimers (R=0.77).

99 SC3-2, "photooxidation"

100 **Temporal behavior:** SC3-2 is a daytime factor reaching maximum at 13:00 when it is responsible for approximately 50%
101 of the measured signal in this range (Fig. S7). Due to diurnal variation, SC3-2 is most likely terminated by NO.

102 **Spectral features:** The mass spectrum of SC3-2 is noisy and without a visible pattern (Fig. S5), thus the oxidant is most
103 likely not chemoselective. That points at OH as the main oxidant. Nevertheless, O₃ could also act as an oxidant. SC3-2
104 contains HOM with 19 carbons, though identification of many key compounds is hindered by the low S/N ratio. SC3-2
105 contains HOM, noise, and F-impurities.

106 **Other:** SC3-2 correlates with many other factors at the street canyon. It has the highest correlation with SC2-1: MT
107 monomers 1 (R=0.88) and it also correlates with UB1-6: C7-8 (R=0.77).

108 • Not selected factors

109 The timeseries, spectra and diurnal profiles for "not selected" factors at UB can be found in Figure S9.

110 SC1-1, "nitrophenol 1"

111 **Temporal behavior:** SC1-1 is daytime factor with maximum at 13:00. Diurnal variation suggests that OH or O₃ are
112 oxidants involved in the formation of this factor.

113 **Spectral features:** SC1-1 consists of C₆H₅O₃N, C₇H₇O₃N, C₆H₅O₃NHNO₃, C₁₀H₁₅O₈N. The mass spectrum contains
114 mainly nitrophenol, which suggests an anthropogenic origin of SC1-1. SC1-1 includes ONCs, which implies an
115 involvement of NO_x.

116 **Other:** SC1-1 correlates with many factors at street canyon: SC1-2: MT monomers 3 (R=0.92), SC2-1: MT monomers 1
117 (R=0.87), and SC3-2: photooxidation (R=0.86) as well as with UB2-4: MT monomers 3 (R=0.66)

118 **Reason for not “selecting”:** SC1-1 has very similar temporal trend to other factors in this range at the street canyon. As
119 PMF solutions are less reliable for this m/Q range at street canyon, we did not want to put too much focus on this factor.

120 **SC1-2, "MT monomers 3"**

121 **Temporal behavior:** SC1-2 is a daytime factor with a maximum at 13:00, which suggests that OH or O₃ are involved in
122 the formation of this factor.

123 **Spectral features:** SC1-2 contain C₇H₁₀O₄, C₉H₁₅O₆N, C₁₀H₁₅O₇N, C₁₀H₁₇O₇N or C₁₀H₁₅O₈, and C₁₀H₁₅O₈N, suggesting
124 the biogenic origin of VOCs: MT. SC1-2 often contains ONCs, implying an involvement of NO.

125 **Other:** SC1-2 correlates with *SC1-1: nitrophenol 1* (R=0.87), *SC2-1: MT monomers 1* (R=0.79), *SC3-2: photooxidation*
126 (R=0.71), and with *UBI-6: C7-8* (R=0.63). Factor SC1-2 is very similar to SC1-1.

127 **Reason for not “selecting”:** SC1-2 has very similar temporal trend to other factors in this range at the street canyon. As
128 PMF solutions are less reliable for this m/Q range at street canyon, we did not put too much focus on this factor.

129 **SC1-3, "unidentified 1"**

130 **Temporal behavior:** SC1-3 is a factor elevated from 12:00 to 23:00. That suggests O₃ as the most dominant oxidant.

131 **Spectral features:** SC1-3 contains nitrophenol and only a few peaks from which we cannot identify any compound with
132 certainty.

133 **Other:** SC1-3 correlates with *SC3-2: photooxidation* (R=0.67) and *UBI-6: C7-8* (R=0.74).

134 **Reason for not “selecting”:** SC1-3 has very similar temporal trends to other factors in this range at the street canyon. As
135 PMF solutions are less reliable for this m/Q range at street canyon, we did not put too much focus on this factor.
136 Additionally, we were not able to identify key compounds for this factor and that makes interpretation of SC1-3 limited.

137 **SC1-4, "unidentified 2"**

138 **Temporal behavior:** SC1-4 is a factor elevated during most of the time except between 16:00 and 21:00 (Fig. S9).

139 **Spectral features:** SC1-4 contains nitrophenol. We cannot identify any other key compounds for SC1-4.

140 **Other:** SC1-4 correlates with *SC2-2: 370+433* (R=0.62), CO₂ (R=0.50).

141 **Reason for not “selecting”:** SC1-4 has very similar temporal trends to other factors in this range at the street canyon. As
142 PMF solutions are less reliable for this m/Q range at street canyon, we did not put too much focus on this factor.
143 Additionally, we were not able to identify key compounds for this factor and that makes interpretation of SC1-4 limited.

144 **SC1-5, "nitrophenol & aliphatic"**

145 **Temporal behavior:** SC1-5 is a daytime factor with a maximum at 2 p.m. (Fig. S9), which suggests OH or O₃ as the
146 main oxidant.

147 **Spectral features:** SC1-5 contains: C₆H₅O₃N, C₅H₇O₆N, C₆H₉O₆N, C₆H₁₁O₆N, C₇H₁₁O₆N, C₇H₉O₇N and/or C₈H₁₃O₆N,
148 C₆H₁₀O₈N₂, C₇H₁₂O₈N₂ or C₈H₁₂O₉, C₈H₁₂O₉N₂ or C₉H₁₄O₉N. Key compounds include nitrophenol as well as ions
149 previously detected in China and identified as the product of oxidation of aliphatic VOCs (Guo et al., 2022; Liu et al.,

150 2021), implying that SC1-5 is formed of anthropogenic VOCs. Almost all key compounds are ONCs suggesting an
151 involvement of NO in the formation of SC1-5. There is no clear pattern in a mass spectrum (Fig. S9), suggesting that the
152 main oxidant is not chemoselective: OH.

153 **Other:** SC1-5 correlates with *SC2-1: MT monomers 1* (R=0.70) and *UB1-2: nitrophenol* (R=0.63)

154 **Reason for not “selecting”:** SC1-5 has very similar temporal trends to other factors in this range at the street canyon. As
155 PMF solutions are less reliable for this m/Q range at street canyon, we did not put too much focus on this factor.

156 **SC2-4, "unidentified 3"**

157 **Temporal behavior:** SC2-4 is a daytime factor with a maximum at 14:00 (Fig. S9), which suggests OH or O₃ as the main
158 oxidant.

159 **Spectral features:** Factor SC2-4 has similar time series to factors SC2-1 and SC2-2, which makes it impossible to
160 determine a molecular composition of key compounds. The oxidant is most likely not chemoselective towards VOCs,
161 which suggests OH as the most dominant oxidant (Fig. S9). However, O₃ may also play a role as an oxidant for SC2-4
162 formation.

163 **Other:** SC2-4 correlates with *SC2-3: MT monomers 2* (R=0.64) and *UB1-6: C7-8* (R=0.56).

164 **Reason for not “selecting”:** We were not able to identify key compounds for this factor as it has too similar temporal
165 behavior with SC2-1 and SC2-2. This makes interpretation of SC2-4 limited.

166 **SC2-5, "unidentified 4"**

167 **Temporal behavior:** SC2-5 is a daytime factor with a maximum at 14:00 (Fig. S9), which suggests OH or O₃ as the main
168 oxidant.

169 **Spectral features:** SC2-5 is driven mostly by one peak at 355 Th. The lack of a pattern in the mass spectrum (Fig. S9)
170 indicate an oxidant which is not chemoselective towards VOCs precursors, thus most likely this factor is formed through
171 OH oxidation. O₃ could also partly participate in formation of this factor.

172 **Other:** SC2-5 correlates with *SC1-2: MT monomers 3* (R=0.67), and *UB2-5: photooxidation 1* (R=0.73)

173 **Reason for not “selecting”:** SC2-5 contains mainly one unidentified peak. Signals of other ions are too small to be
174 determined as key compounds of this factor (Fig. S9).

175 **SC3-3, "unidentified 5"**

176 **Temporal behavior:** SC3-3 has no clear pattern in time series or diurnal variation (Fig. S9).

177 **Spectral features:** Mass spectrum shows only noise (Fig. S9).

178 **Other:** SC3-3 does not have any important correlations.

179 **Reason for not “selecting”:** Mass spectrum and diurnal variation of SC3-3 implies that this factor contains mainly
180 instrumental noise. We did not observe any HOM in this factor.

181 • Urban background station

182 • Selected factors

183 The timeseries of the UB factors are shown in Figure S4, diurnal variation at Figure 4 in main text, and spectra are
184 presented in Figure S6.

185 **UB1-2, "nitrophenol"**

186 **Temporal behavior:** Daytime maximum at 12:00 suggests an involvement of OH (Fig. 4).

187 **Spectral features:** UB1-2 contains mainly C4-10 compounds. The double bond equivalent (DBE) between 2 and 6 of
188 key compounds indicates that some of them may have an aromatic ring (Table S2). UB1-2 includes nitrophenol
189 ($C_6H_5O_3N$), known as a biomass burning combustion tracer as well as a compound formed from benzene and phenol
190 oxidation, which are AVOCs. This suggests that compounds in UB1-2 were formed from AVOCs. There is no clear
191 pattern in the mass spectrum (Fig. S6), which may indicate that the oxidant does not show chemoselectivity towards the
192 type of VOC precursors. This combined with the information from diurnal variation suggests the involvement of OH in
193 oxidation reactions. UB1-2 often contains N, suggesting the participation of NO_x in the termination reaction.

194 **Other:** UB1-2 correlates the best with global radiation ($R=0.60$), which also suggests the participation of OH in oxidation
195 reactions. UB1-2 has a negative correlation with a cosine of wind direction ($R=-0.55$) indicating that this factor is rather
196 coming from south of the station. UB1-2 correlates also with factor *SC2-1: MT monomers 1* ($R=0.75$), and factor *UB2-*
197 *5: photooxidation 1* ($R=0.57$). Correlation with factor UB2-5 could be explained by a similar oxidation mechanism.

198 **UB1-6, "C7-8"**

199 **Temporal behavior:** UB1-6 has a daytime maximum at 17:00 (Fig. 4) showing similarities to the diurnal variation of O_3
200 concentrations. O_3 or OH could be the oxidant for formation of UB1-6.

201 **Spectral features:** UB1-6 contains C7-8 compounds, which were previously reported from MT oxidation with non-zero
202 NO_x concentration (Pullinen et al., 2020; Yan et al., 2020) and in ambient measurement (Liu et al., 2021). At the same
203 time, these compounds were found as HOM formed from aromatic VOCs (Guo et al., 2022). A pattern in the mass
204 spectrum (Fig. S6) suggests chemoselectivity of the oxidant towards VOC precursors implying that O_3 may be the
205 dominant oxidant. UB1-6 contains ONCs, which suggests an involvement of NO.

206 **Other:** UB1-6 correlates with three factors at street canyon: *SC1-3: unidentified 1* ($R=0.74$), *SC2-1: MT monomers 1*
207 ($R=0.66$), and *SC3-2: 370+433* ($R=0.77$). UB1-6, *S1-3: unidentified 1*, and *SC2-1: MT monomers 1* have the same
208 oxidation mechanism. UB1-6 also correlates with temperature ($R=0.76$) and O_3 concentration ($R=0.55$) suggesting O_3 as
209 the main oxidant.

210 **UB2-1, "MT monomers 1"**

211 **Temporal behavior:** UB2-1 is a daytime factor with two maxima: at 5:00 and 21:00 (Fig. 4), which correspond to the
212 time of sunrise and sunset during the measurement period (Fig 2). That suggests that UB1-2 is a factor rather driven by
213 the chemical condition of the atmosphere during these periods of the day and not by local emissions. Unique diurnal
214 variation implies that UB2-1 could be oxidized by nighttime NO_3 and terminated mostly by daytime NO.

215 **Spectral features:** Key compounds contain $C_9H_{14}O_{9,11}N_2$ or $C_{10}H_{16}O_{9,11}N$, and $C_{10}H_{17}O_{12}N_3$ (Table S2), which suggests
216 MT as initial VOCs. UB2-1 contains N, which suggests an involvement of one or both reagents leading to ONCs: NO
217 and NO_3 .

218 **Other:** UB2-1 does not correlate with any other factor or analyzed parameter.

219 **UB2-2, "MT monomers 2"**

220 **Temporal behavior:** UB2-2 has the highest concentrations during the nighttime with a maximum at 21:00, however, it
221 has also a daytime local maximum at 11:00. (Fig. 4). Since UB2-2 is mostly present during nighttime, OH probably does
222 not play an important role in oxidation. The drop in the concentration in the morning corresponds to the appearance of
223 NO and increase of another factor at the urban background (UB2-4). NO may act as an inhibitor for UB2-2 partly leading
224 to the formation of UB2-4.

225 **Spectral features:** Key compounds of UB2-2 contain $C_{10}H_{15}O_{9-11}N$, $C_9H_{14}O_{10}N_2$, $C_9H_{15}O_{11}N_3$, and $C_9H_{15}O_9N_2$ or
226 $C_{10}H_{17}O_9N$ (Table S2), which indicates that this factor is formed from biogenic VOCs - MT. Since all key compounds
227 are ONCs and NO rather acts as an inhibitor, not terminator, UB2-2 is mostly likely oxidized by NO_3 . However, we
228 cannot exclude some participation from O_3 in oxidation.

229 **Other:** UB2-2 correlates with *UB3-2: MT dimers* ($R=0.65$) and *SC2-3: MT monomers 2* ($R=0.56$). Since *UB3-2: MT*
230 *dimers* contain MT dimers, UB2-2 could be also terminated by RO_2 . UB2-2 has a negative correlation with NO_x ($R=$
231 0.45) suggesting that NO is not participating in termination reactions.

232 **UB2-3, "sesquiterpene 1"**

233 **Temporal behavior:** UB2-3 is a nighttime factor with a maximum at 23:00 (Fig. 4), thus NO_3 or O_3 is most likely the
234 oxidant and UB2-3 is formed during the absence of NO.

235 **Spectral features:** Key compounds of this factor contain $C_{15}H_{23}O_{8,10,12-13}N$ and $C_{15}H_{24}O_{13}N$ (or $C_{15}H_{23}O_{10}NHNO_3$) (Table
236 S2), implying that this factor is formed from biogenic VOCs- sesquiterpenes. UB2-3 often contains N, which suggests an
237 involvement of NO_3 . O_3 could also participate in oxidation.

238 **Other:** UB2-3 correlates with *UB3-1: sesquiterpene 2* ($R=0.93$).

239 **UB2-4, "MT monomers 3"**

240 **Temporal behavior:** UB2-4 is a daytime factor with a maximum at 7:00 (Fig. 4), which suggests NO as the main
241 terminator for the formation mechanism. Either oxidant could be responsible for the formation of that factor, however,
242 O_3 and OH are more likely due to their diurnal behavior.

243 **Spectral features:** The main peaks present in the mass spectrum are $C_{10}H_{16}O_9N_2$ (370 Th) and $C_{10}H_{16}O_9N_2HNO_3$ (433
244 Th). The key compounds contain $C_9H_{14}O_{10}N_2$, $C_{10}H_{16}O_{10}$, $C_{10}H_{16}O_{11}N$, $C_{10}H_{16}O_9N_2$ and $C_{10}H_{16}O_9N$ or $C_9H_{14}O_9N_2$ (Table
245 S2), which suggests the biogenic origin of the VOC precursors: MT.

246 **Other:** It correlates with *SC1-1: nitrophenol 1* ($R=0.66$), *SC2-2: 370+433* ($R=0.75$), and NO_2 ($R=0.61$).

247 **UB2-5, "photooxidation 1"**

248 **Temporal behavior:** UB2-5 is a daytime factor with a maximum at 12:00 (Fig. 4), at that time it corresponds to more
249 than 50% of the signal at this range (Fig. S8). The diurnal variation suggests that UB2-5 is oxidized mainly by OH.

250 **Spectral features:** The mass spectrum of UB2-5 has no clear pattern in it, which suggests OH as the main oxidant (Fig.
251 S6). Due to the low signal-to-noise ratio, there are only two HOM, ONCs, identified as key ions: $C_{10}H_{11}O_9N$ and
252 $C_{10}H_{16}O_9N_2$ (Table S2). The presence of ONCs suggests that HOM in UB2-5 are terminated by NO. UB2-5 most likely
253 contains VOCs oxidized by OH and a noise. We cannot exclude O_3 as an oxidant for this factor.

254 **Other:** UB2-5 correlates with *UB3-3: photooxidation 2* ($R=0.77$), and relative humidity ($R=0.77$). UB2-5 and UB3-3 are
255 formed most likely by the oxidation with OH.

256 **UB3-1, "sesquiterpene 2"**

257 **Temporal behavior:** UB3-1 is a nighttime factor with a maximum at 22:00 (Fig. 4). The highest concentrations of UB3-
258 1 correspond to the time when NO is absent, thus NO works as an inhibitor for this factor. As UB3-1 is a nighttime factor,
259 OH is not involved in the oxidation.

260 **Spectral features:** Key compounds contain $C_{15}H_{23}O_{10-13}N$ and $C_{15}H_{23}O_{14-16}NHNO_3$ (or $C_{15}H_{24}O_{13-16}N_2$) (Table S2), which
261 suggests a biogenic origin of VOCs, likely sesquiterpenes based on the number of C and H. The presence of ONC implies
262 that UB3-1 is formed by NO_3 oxidation, however, we cannot exclude O_3 as an oxidant.

263 **Other:** UB3-1 correlates with *UB2-3: sesquiterpene 1* ($R=0.93$).

264 **UB3-2, "MT dimers "**

265 **Temporal behavior:** UB3-2 is a nighttime factor staying elevated between 23:00 and 3:00 (Fig. 4), which suggests that
266 OH is not involved in oxidation. UB3-2 is present when the NO is absent implying that NO acts as an inhibitor for this
267 factor.

268 **Spectral features:** UB3-2 contains as key compounds dimers of MT: $C_{20}H_{32}O_{13-16}N_2$, $C_{20}H_{31}O_{13}N$, and possibly
269 $C_{20}H_{30}O_{14}N$, $C_{18}H_{26}O_{15-16}$, $C_{17}H_{26}O_{14-15}N_2$ (Table S2). Since UB3-2 contains dimers, the formation of this factor must be
270 terminated by RO_2 . The presence of ONC implies that NO_3 is the main oxidant, however, O_3 could also be involved in
271 oxidation reactions.

272 **Other:** UB3-2 correlates with *UB2-2: photooxidation 1* ($R=0.65$), *SC3-1: MT dimers* ($R=0.77$).

273 **UB3-3, "photooxidation 2"**

274 **Temporal behavior:** UB3-3 is a daytime factor with a maximum at 12:00, which represents 60% of the measured signal
275 at this range during morning and noon (Fig. S8). The diurnal variation suggests that UB3-1 is oxidized mainly by OH.

276 **Spectral features:** The mass spectrum of UB3-3 is noisy and does not show any pattern (Fig. S6), implying not
277 chemoselective main oxidant: OH. The only compounds identified in this factor were F-impurities. Since UB3-3
278 sometimes contains more than 50% of the measured signal, we suspect that it also contains HOM which we cannot identify
279 due to the low S/N ratio.

280 **Other:** UB3-3 correlates with *UB2-5: photooxidation 1* ($R=0.77$) and relative humidity ($R=0.57$).

281 • Not selected factors

282 The timeseries, spectra and diurnal profiles for “not selected” factors at UB can be found in Figure S10.

283 **UB1-1, “Water clusters”**

284 **Temporal behavior:** Nighttime maximum at 4:00. Present only periodically. The time series and the diurnal variation
285 correspond to the time series and diurnal variation of water clusters confirming that UB1-1 contains mostly isotopes of
286 water clusters.

287 **Spectral features:** The mass spectrum of factor UB1-1 contains mostly m/Q 1 and 2 Th higher than m/Q of removed
288 water clusters (Fig. S10). Key compounds of that spectrum were identified as isotopes of water clusters.

289 **Other:** UB1-1 correlates with RH (R= 0.63).

290 **Reason for not “selecting”:** UB1-1 contains only isotopes of water clusters, an artefact.

291 **UB1-3, "unidentified 1"**

292 **Temporal behavior:** UB1-3 has two maxima: daytime at 13:00 and nighttime at 23:00 (Fig. S10), suggesting that
293 atmospheric condition at the station does not drive that factor.

294 **Spectral features:** UB1-3 is never a dominant factor during the campaign and its key compounds correspond to key
295 compounds of other factors from this range; thus, the only key compound identified is C₉H₁₄O₈N₂. It is likely that either
296 NO, NO₃, or both are involved in the formation of UB1-3. We cannot identify which oxidant participates in the formation
297 of that factor. However, the lack of a pattern in mass spectrum may indicate that the oxidant is not chemoselective towards
298 VOC precursors (Fig. S10). This makes O₃ the less likely oxidant to participate in the formation of B1-3.

299 **Other:** UB1-3 correlates with *UB2-2: MT monomers 1* (R=0.61) and *SCI-2: MT monomers 3* (R=0.61).

300 **Reason for not “selecting”:** UB1-3 is never a dominant factor, and its key compounds correspond to key compounds of
301 other factors from this range; thus, we were able to identify only one compound. This makes interpretation of UB1-3
302 limited.

303 **UB1-4, "unidentified 2"**

304 **Temporal behavior:** UB1-4 has a maximum at 5:00 and it reaches the lowest concentrations between 8:00 and 13:00
305 (Fig. S10). The diurnal variation suggests that NO does not participate in the termination reaction of that factor.

306 **Spectral features:** Mass spectrum of UB1-4 is dominated by only a few peaks from which we cannot certainly identify
307 any compound.

308 **Other:** UB1-4 has a negative correlation with *UB1-5: unidentified 3* (R=-0.59).

309 **Reason for not “selecting”:** We are not able to undoubtedly identify any compound in UB1-4.

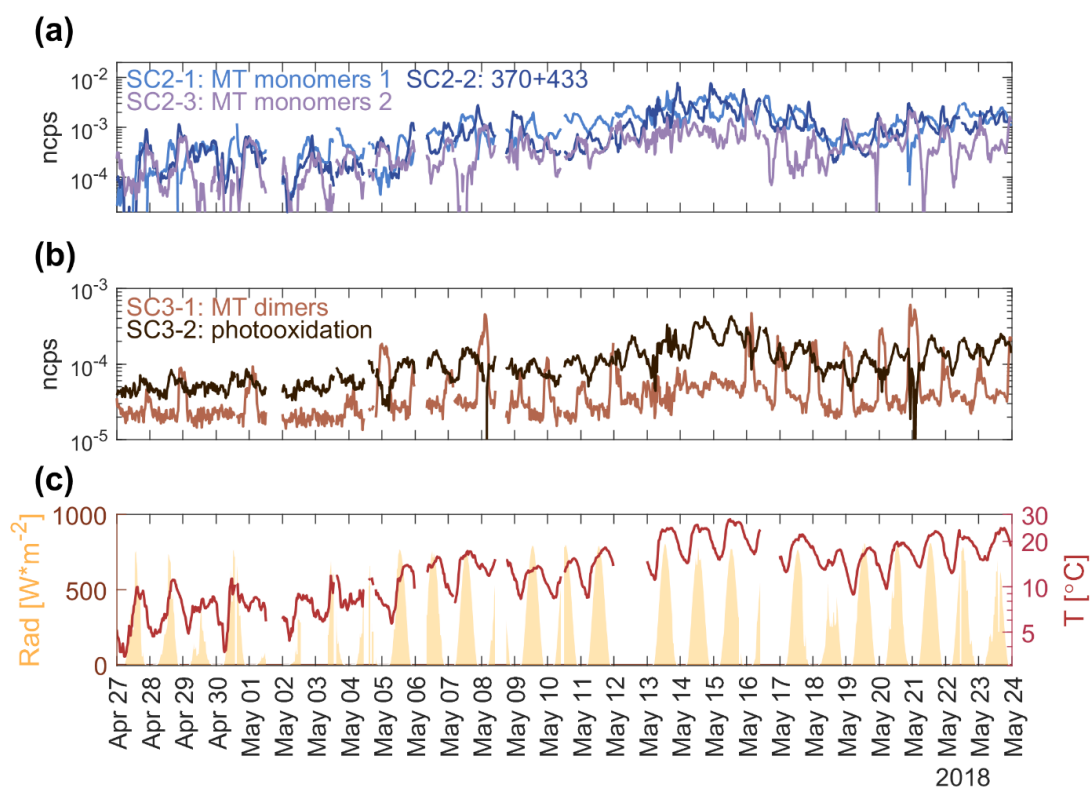
310 **UB1-5, "unidentified 3"**

311 **Temporal behavior:** UB1-5 is a daytime factor elevated between 10:00 and 16:00 (Fig. S10). That suggests an
312 involvement of O₃ or OH in the oxidation. Diurnal variation of B1-5 shows higher concentrations when NO is present at
313 the background station (Fig. S10 and Fig. 2).

314 **Spectral features:** UB1-5 is a daytime factor with a mass spectrum mostly driven by one m/Q (261 Th, Fig. S10), which
315 cannot be identified. The only compound which we can certainly identify is C₁₀H₁₆O₈N (339 Th). The mass spectrum
316 contains several more pronounced peaks with odd m/Q which could be radicals, or due to the nitrogen rule, ONC with an
317 odd number of nitrogen molecules. HOM in UB1-5 may be terminated by NO or HO₂, but NO is presumably the one
318 terminator more involved in the HOM formation. There is no clear pattern in the mass spectrum (Fig. S10), which may
319 indicate that the oxidant is not chemoselective towards VOC precursors. This suggests OH as more likely oxidant than
320 O₃.

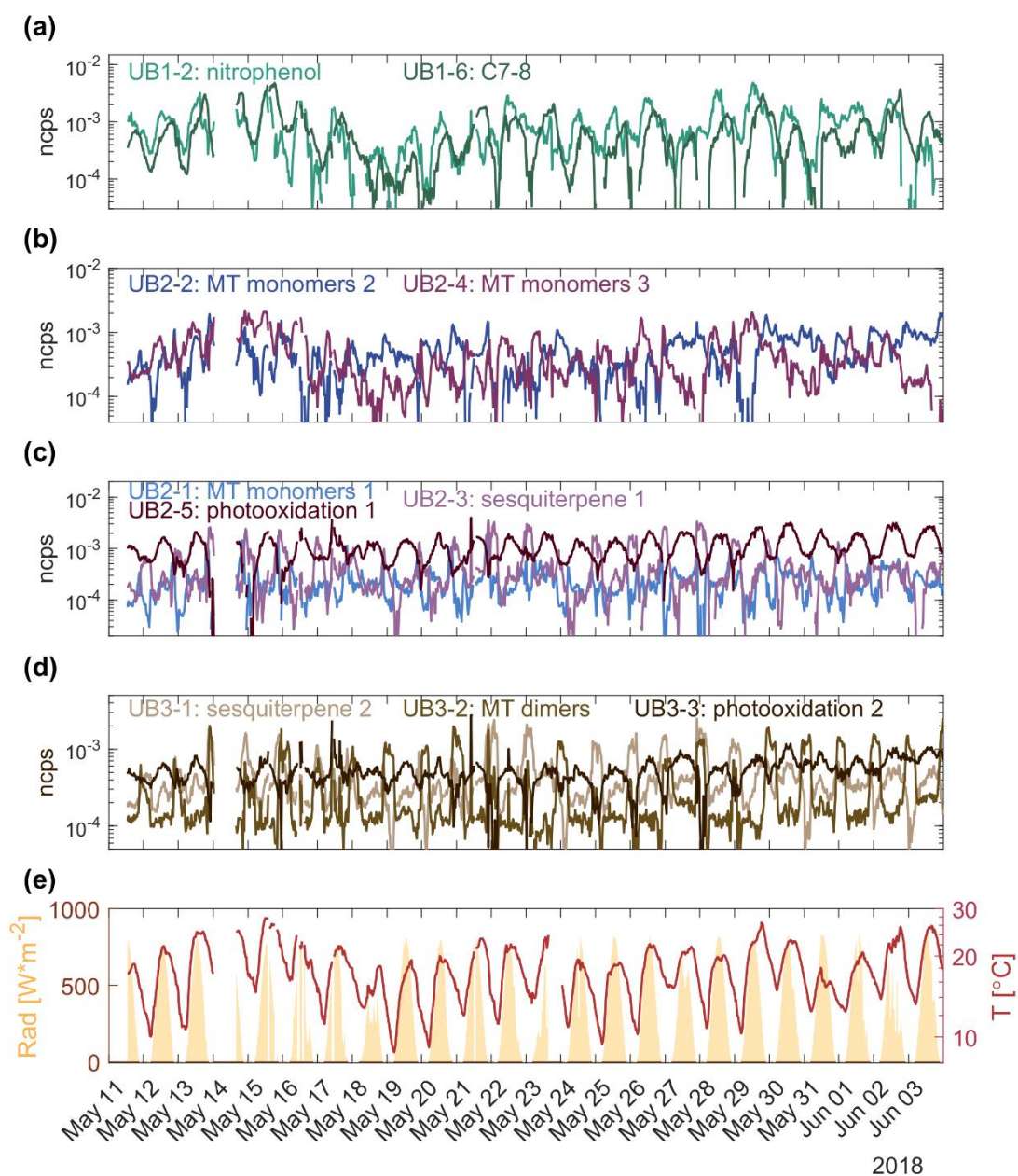
321 **Other:** UB1-5 correlates with *UB2-5: photooxidation 1* (R=0.58) and *SC2-1: MT monomers 1* (R=0.70)

322 **Reason for not “selecting”:** We are not able to undoubtedly identify most of the key compounds in UB1-5.



324

325 Figure S3. Time series of selected PMF factors (a-b) as well as ambient temperature and global radiation (c) at the street
 326 canyon (SC). PMF factors are labeled as SCX-Y where X stands for the analyzed m/Q range (1, 2, or 3), and Y is the
 327 identifying number of the factor in that range. The label of a factors is followed up by a descriptive name.



328

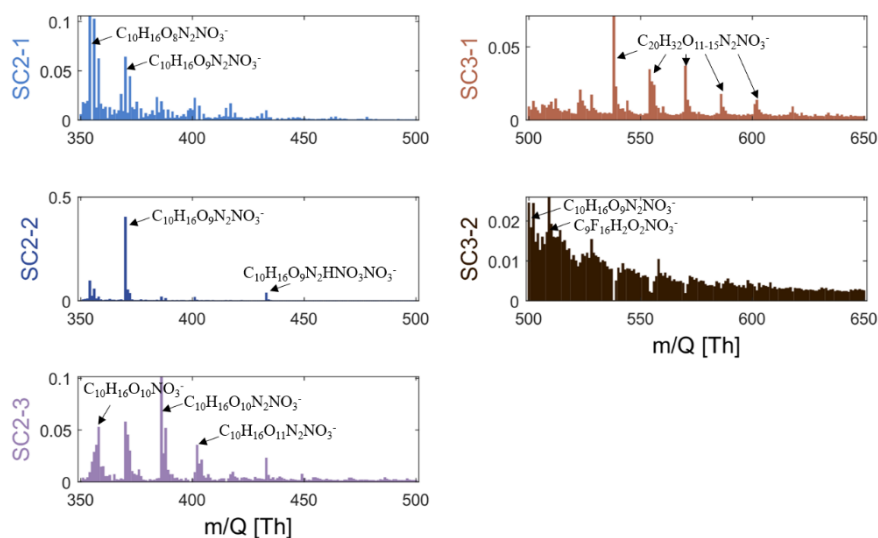
329 Figure S4. Time series of selected PMF factors (a-d) as well as ambient temperature and global radiation (e) at the urban
 330 background station (UB). PMF factors are labeled as UBX-Y where X stands for the analyzed m/Q range (1, 2, or 3), and
 331 Y is the identifying number of the factor in that range. The label of a factors is followed up by a descriptive name.

332 S6. Chemical composition of selected factors

333 Table S2. Representative peaks identified in the selected factors at the street canyon (SC) and at the urban background
 334 (UB) stations.

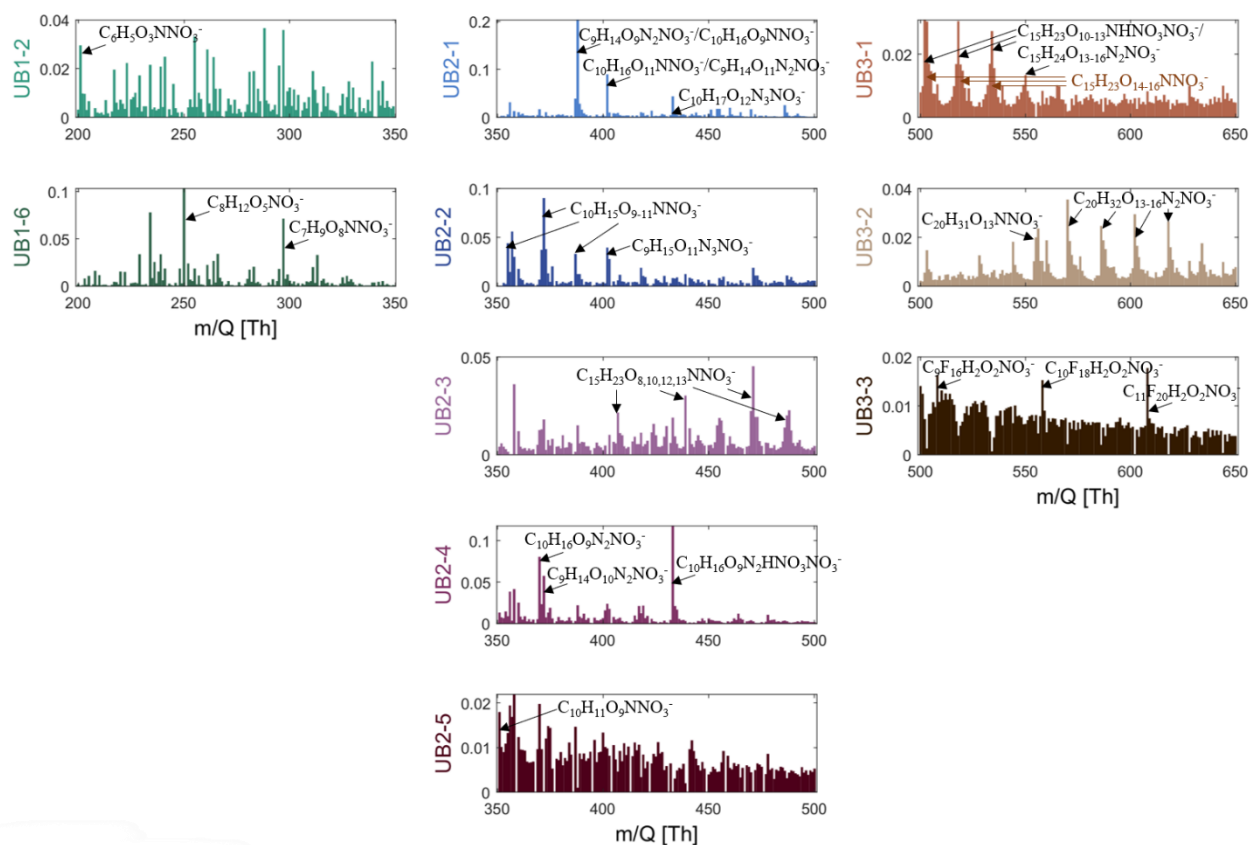
Range [Th]	Factor	Composition
Street canyon		
350-500	SC2-1: MT monomers 1	354: C ₁₀ H ₁₆ O ₈ N ₂ NO ₃ - 356: C ₉ H ₁₄ O ₉ N ₂ NO ₃ - or/and C ₁₀ H ₁₆ O ₉ NNO ₃ - 358: C ₉ H ₁₆ O ₉ N ₂ NO ₃ - or/and C ₁₀ H ₁₆ O ₁₀ NO ₃ - 370: C ₁₀ H ₁₆ O ₉ N ₂ NO ₃ - 372: C ₁₀ H ₁₆ O ₁₀ NNO ₃ - or/and C ₉ H ₁₄ O ₁₀ N ₂ NO ₃ -
	SC2-2: 370+433	370: C ₁₀ H ₁₆ O ₉ N ₂ NO ₃ - 433: C ₁₀ H ₁₆ O ₉ N ₂ NO ₃ HNO ₃ -
	SC2-3: MT monomers 2	358- C ₁₀ H ₁₆ O ₁₀ NO ₃ - 386- C ₁₀ H ₁₆ O ₁₀ N ₂ NO ₃ - 402- C ₁₀ H ₁₆ O ₁₁ N ₂ NO ₃ -
500-650	SC3-1: MT dimers	538: C ₂₀ H ₃₂ O ₁₁ N ₂ NO ₃ - 554: C ₂₀ H ₃₂ O ₁₂ N ₂ NO ₃ - 570: C ₂₀ H ₃₂ O ₁₃ N ₂ NO ₃ - 586: C ₂₀ H ₃₂ O ₁₄ N ₂ NO ₃ - 602: C ₂₀ H ₃₂ O ₁₅ N ₂ NO ₃ -
	SC3-2: photooxidation	500: C ₁₉ H ₂₂ O ₁₀ N ₂ NO ₃ - 502: C ₁₉ H ₂₄ O ₁₀ N ₂ NO ₃ - 508: C ₉ F ₁₆ H ₂ O ₂ NO ₃ - 558: C ₁₀ F ₁₈ H ₂ O ₂ NO ₃ -
	Urban background station	
200-350	UB1-2: nitrophenol	201: C ₆ H ₅ O ₃ NNO ₃ - 217: C ₆ H ₅ O ₄ NNO ₃ - 234: C ₇ H ₈ O ₅ NO ₃ - 241: C ₄ H ₅ O ₇ NNO ₃ - 288: C ₁₀ H ₁₀ O ₆ NO ₃ - or C ₆ H ₁₀ O ₉ NO ₃ -
	UB1-6: C7-8	250: C ₈ H ₁₂ O ₅ NO ₃ - 297: C ₇ H ₉ O ₈ NNO ₃ - 313: C ₈ H ₁₃ O ₈ NNO ₃ - or C ₈ H ₁₂ O ₅ HNO ₃ NO ₃ -
350-500	UB2-1: MT monomers 1	356: C ₉ H ₁₄ O ₉ N ₂ NO ₃ - or C ₁₀ H ₁₆ O ₉ NNO ₃ - 388: C ₁₀ H ₁₆ O ₁₁ NNO ₃ - or C ₉ H ₁₄ O ₁₁ N ₂ NO ₃ - 433: C ₁₀ H ₁₇ O ₁₂ N ₃ NO ₃ -
	UB2-2: MT monomers 2	355: C ₁₀ H ₁₅ O ₉ NNO ₃ - 357: C ₉ H ₁₅ O ₉ N ₂ NO ₃ - or C ₁₀ H ₁₇ O ₉ NNO ₃ - 371: C ₁₀ H ₁₅ O ₁₀ NNO ₃ - 372: C ₉ H ₁₄ O ₁₀ N ₂ NO ₃ - 387: C ₁₀ H ₁₅ O ₁₁ NNO ₃ - 403: C ₉ H ₁₅ O ₁₁ N ₃ NO ₃ -
	B2-3: sesquiterpene 1	407: C ₁₅ H ₂₃ O ₈ NNO ₃ - 439: C ₁₅ H ₂₃ O ₁₀ NNO ₃ - 471: C ₁₅ H ₂₃ O ₁₂ NNO ₃ - 487: C ₁₅ H ₂₃ O ₁₃ NNO ₃ - 488: C ₁₅ H ₂₄ O ₁₃ NNO ₃ -
	UB2-4: MT monomers 3	356: C ₁₀ H ₁₆ O ₉ NNO ₃ - or C ₉ H ₁₄ O ₉ N ₂ NO ₃ - 358: C ₁₀ H ₁₆ O ₁₀ NO ₃ - 370: C ₁₀ H ₁₆ O ₉ N ₂ NO ₃ - 372: C ₉ H ₁₄ O ₁₀ N ₂ NO ₃ - 388: C ₁₀ H ₁₆ O ₁₁ NNO ₃ - 433: C ₁₀ H ₁₆ O ₉ N ₂ NO ₃ HNO ₃ -
	UB2-5: photooxidation 1	351: C ₁₀ H ₁₁ O ₉ NNO ₃ - 370: C ₁₀ H ₁₆ O ₉ N ₂ NO ₃ -
500-650	UB3-1: sesquiterpene 2	502: C ₁₅ H ₂₄ O ₁₃ N ₂ NO ₃ - or C ₁₅ H ₂₃ O ₁₀ NHNO ₃ NO ₃ - 503: C ₁₅ H ₂₃ O ₁₄ NNO ₃ -

	518: $C_{15}H_{24}O_{14}N_2NO_3^-$ or $C_{15}H_{23}O_{11}NHNO_3NO_3^-$
	519: $C_{15}H_{23}O_{15}NNO_3^-$
	534: $C_{15}H_{24}O_{15}N_2NO_3^-$ or $C_{15}H_{23}O_{12}NHNO_3NO_3^-$
	535: $C_{15}H_{23}O_{16}NNO_3^-$
	550: $C_{15}H_{24}O_{16}N_2NO_3^-$ or $C_{15}H_{23}O_{13}NHNO_3NO_3^-$
UB3-2: MT dimers	544: $C_{17}H_{26}O_{14}N_2NO_3^-$ or $C_{18}H_{26}O_{15}NO_3^-$
	555: $C_{20}H_{31}O_{13}NNO_3^-$
	556: $C_{20}H_{30}O_{14}NO_3^-$ or $C_{19}H_{30}O_{13}N_2NO_3^-$
	560: $C_{18}H_{26}O_{16}NO_3^-$ or $C_{17}H_{26}O_{15}N_2NO_3^-$
	570: $C_{20}H_{32}O_{13}N_2NO_3^-$
	586: $C_{20}H_{32}O_{14}N_2NO_3^-$
	602: $C_{20}H_{32}O_{15}N_2NO_3^-$
	618: $C_{20}H_{32}O_{16}N_2NO_3^-$
UB3-3: photooxidation 2	508: $C_9F_{16}H_2O_2NO_3^-$
	558: $C_{10}F_{18}H_2O_2NO_3^-$
	608: $C_{11}F_{20}H_2O_2NO_3^-$



335

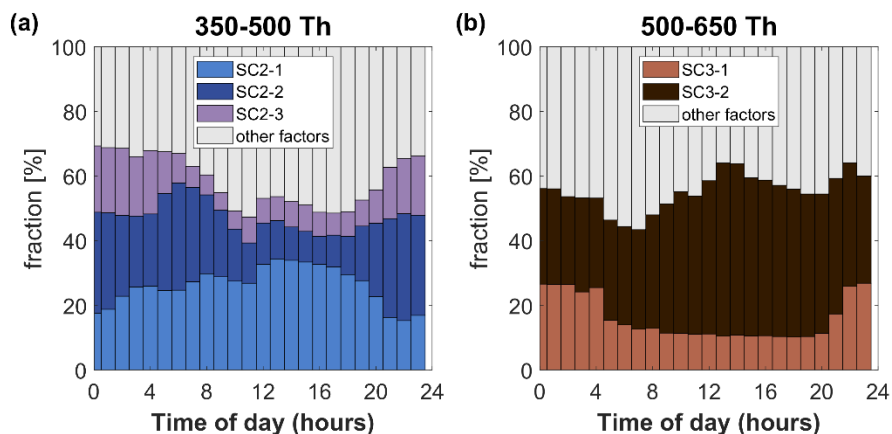
336 Figure S5. Mass spectra of selected PMF factors at the street canyon (SC). PMF factors are labeled as SCX-Y where X
 337 stands for the analyzed m/Q range (2 or 3), and Y is the identifying number of the factor in that range. The left panel
 338 contains mass spectra for range 350-500 Th, and the right one for 500-650 Th.



339

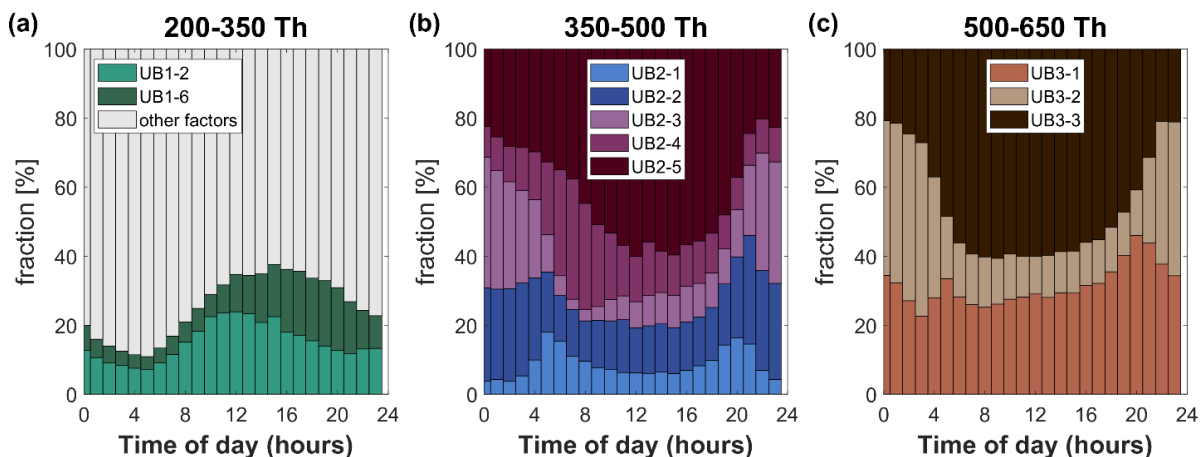
340 Figure S6. Mass spectra of selected PMF factors at the urban background station (UB). Left panel contains mass spectra
 341 for range 200-350 Th, middle one for 350-500 Th, and the right one for 500-650 Th. PMF factors are labeled as UBX-Y
 342 where X stands for the analyzed m/Q range (1, 2, or 3), and Y is the identifying number of the factor in that range.

343 **S7. Ion fractions of selected factors**



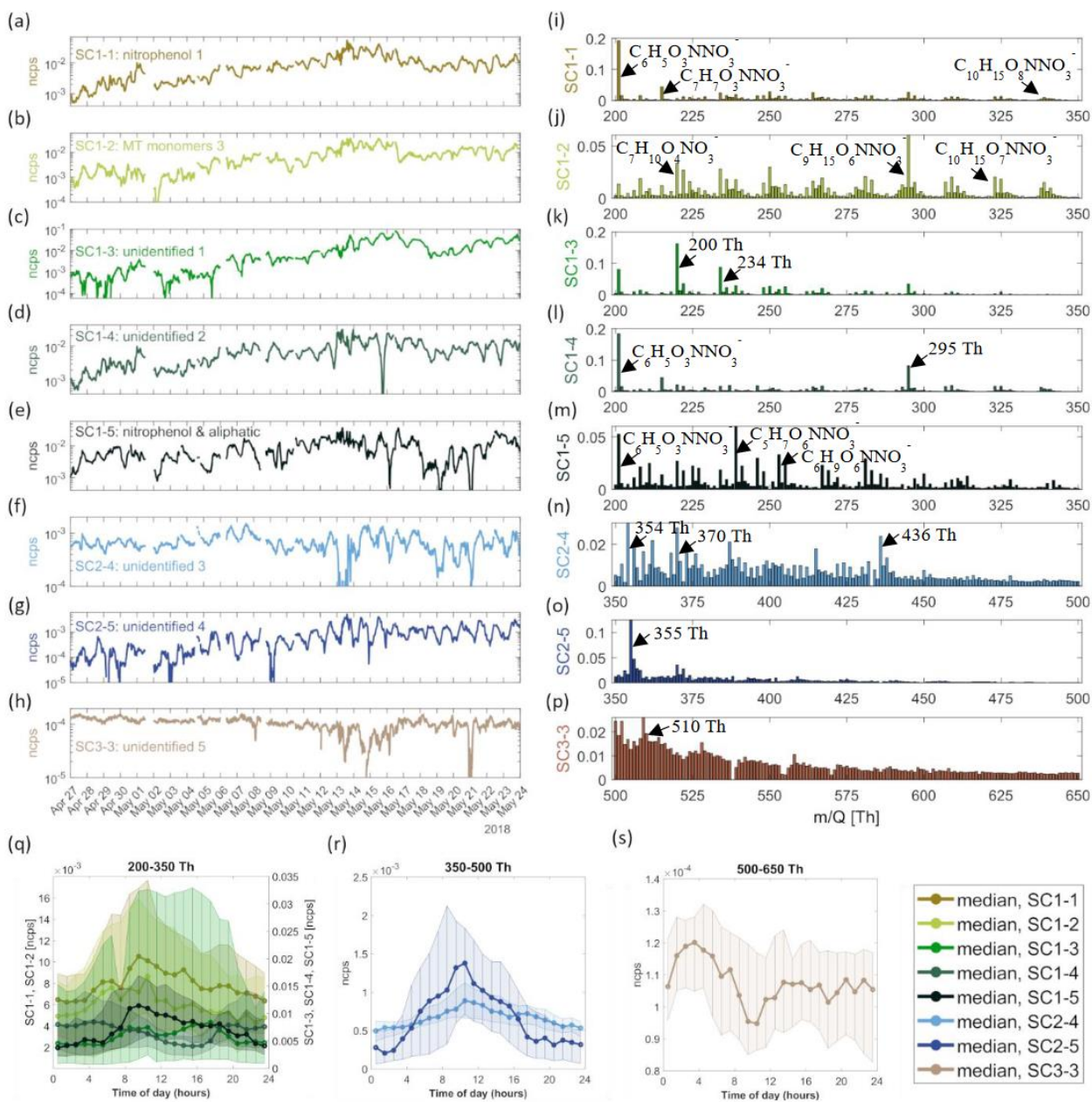
344

345 Figure S7. Diurnal variation of the selected factor fractions at street canyon (SC). The left panel contains variation for
 346 range 350-500 Th, and the right one for 500-650 Th. PMF factors are labeled as SCX-Y where X stands for the analyzed
 347 m/Q range (2 or 3), and Y is the identifying number of the factor in that range.



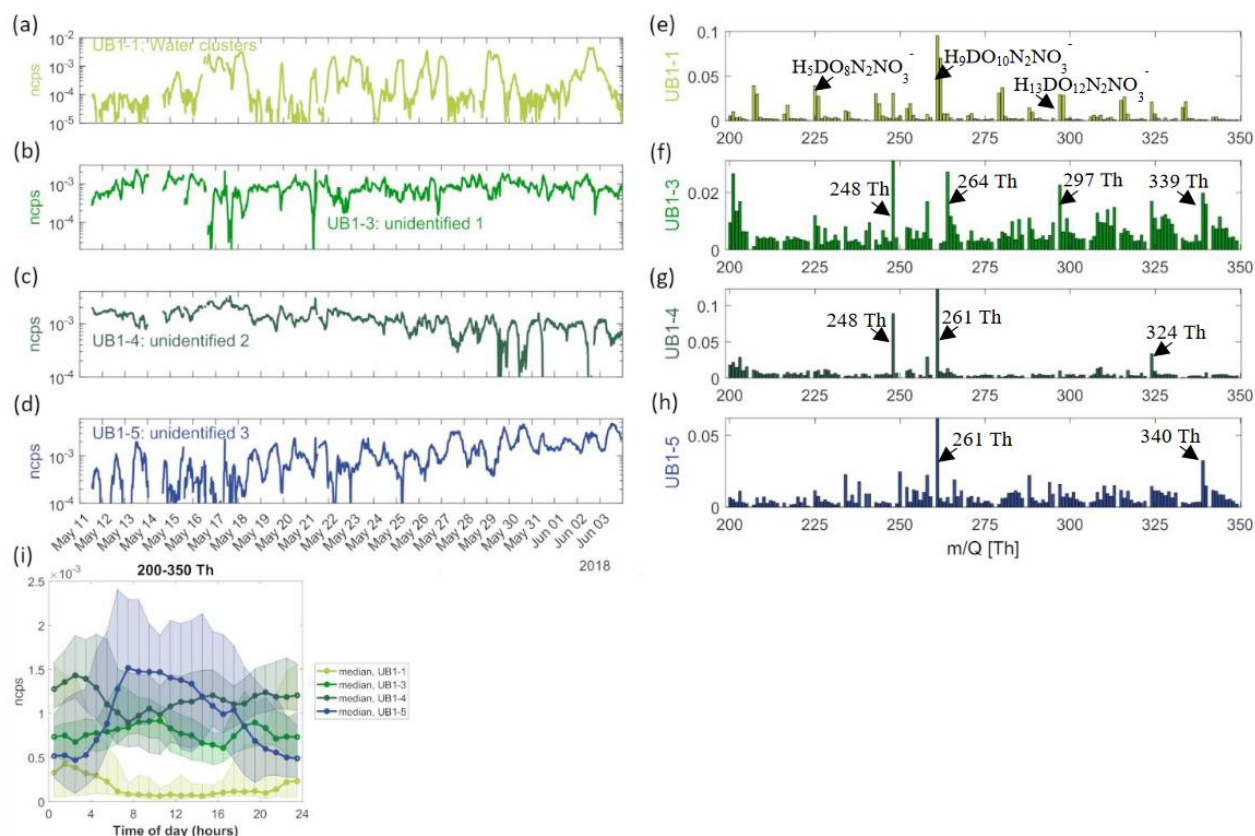
348

349 Figure S8. Diurnal variation of the selected factor fractions at urban background station (UB). The left panel contains
 350 variation for range 200-350 Th, middle one for 350-500 Th, and the right one for 500-650 Th. PMF factors are labeled as
 351 UBX-Y where X stands for the analyzed m/Q range (1, 2, or 3), and Y is the identifying number of the factor in that
 352 range.



354

355 Figure S9. Time series of not selected PMF factors (a-h), their mass spectra (i-p), and diurnal variation (q-s) at the street
 356 canyon (SC). PMF factors are labeled as SCX-Y where X stands for the analyzed m/Q range (1, 2, or 3), and Y is the
 357 identifying number of the factor in that range. The label of a factors is followed up by a descriptive name. The median
 358 diurnal variation is shown as a solid line with markers; the 25th and 75th percentile ranges are presented as shaded areas.



359

360 Figure S10. Time series of not selected PMF factors (a-d), their mass spectra (e-h), and their diurnal variation (i) at the
 361 urban background station (UB). PMF factors are labeled as UBX-Y where X stands for the analyzed m/Q range (1), and
 362 Y is the identifying number of the factor in that range. The label of a factors is followed up by a descriptive name. The
 363 median diurnal variation is shown as a solid line with markers; the 25th and 75th percentile ranges are presented as shaded
 364 areas.

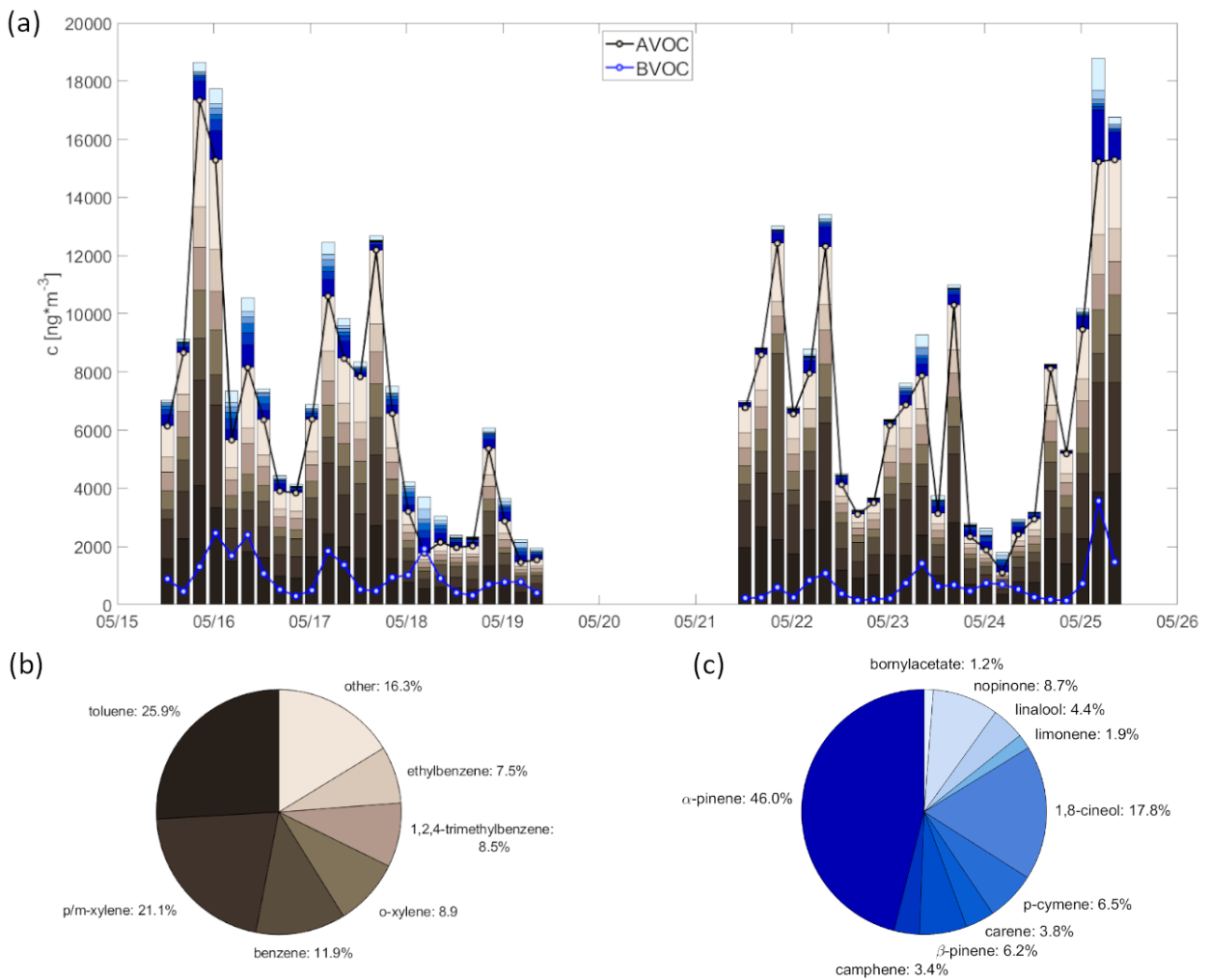
365 Table S3. Suggested characterization of not selected factors at both stations. The table contains information about
 366 probable precursors, oxidants, terminators of formation mechanisms for HOM as well as information about diurnal
 367 variation profile (daytime (D) and nighttime (N)), fraction percentage (%) and potential inhibitors for factors. The
 368 possibility of influence of a variable on factor is marked by yes, M (maybe), or no.

Range [Th]	Factor	Precursor	Oxidant			Terminator			Diurnal peak time	Fraction %	
			OH	NO ₃	O ₃	NO	RO ₂	HO ₂		all	range
Street canyon											
	SC1-1 ^{MS}	AVOCs	M	no	M	M	no	M	9	18.8	20.5
	SC1-2 ^{MS}	BVOCs	M	no	M	yes	no	M	10	15.8	17.3
200-350	SC1-3	AVOCs	M	no	M	no	no	M	17	24.9	27.3
	SC1-4	VOCs	M	M	no	yes	no	M	4	15.1	16.4
	SC1-5 ^{MS}	AVOCs	yes	no	M	yes	no	M	9	16.9	18.5
350-500	SC2-4	VOCs	yes	no	M	M	no	M	10	1.4	17.1
	SC2-5	VOCs	yes	no	M	M	no	M	10	1.5	19.5
500-650	SC3-3	noise	-	-	-	-	-	-	3	0.2	39.0
Background station											

369

200-350	UB1-1	Water clusters	-	-	-	-	-	-	1	5.3	9.2
	UB1-3	VOCs	yes	yes	M	yes	no	M	10	8.8	16.3
	UB1-4	VOCs	M	M	M	no	no	M	2	13.1	24.2
	UB1-5	VOCs	yes	no	M	yes	no	M	7	12.5	21.3

370 **S9. Overview of the measured VOCs at the street canyon**

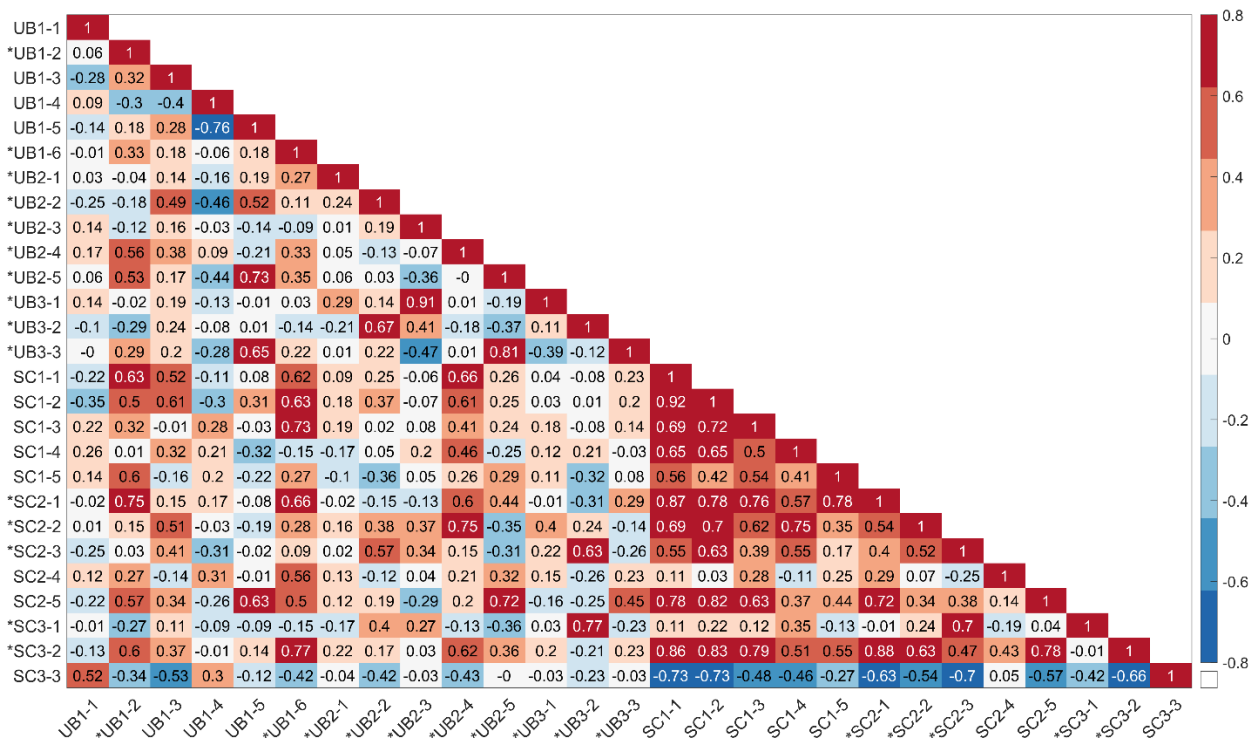


371

372 Figure S11. Time series of measured VOCs concentrations (a) and the fraction of an individual AVOC (b) and BVOC (c)
 373 at street canyon. BVOCs and AVOCs which do not make more than 5% of corresponding total BVOC and total AVOC
 374 concentrations are group as “others”.

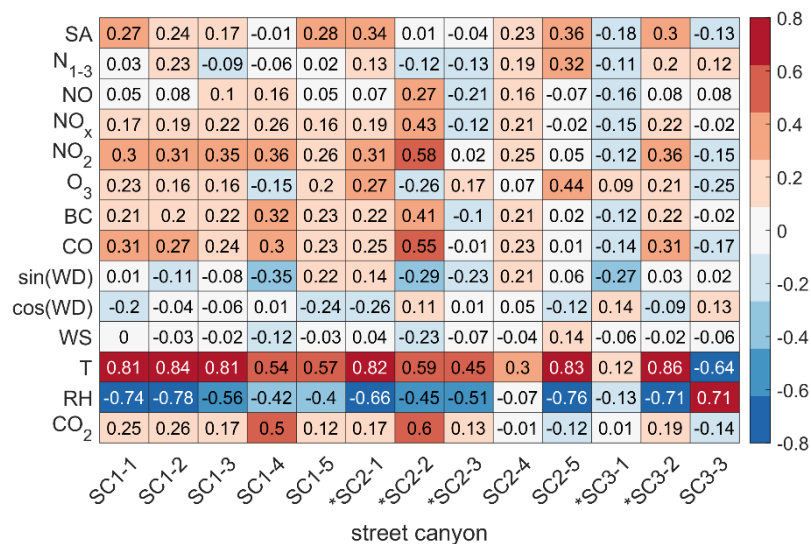
375 **S10. Correlations of observed factors**

376



377

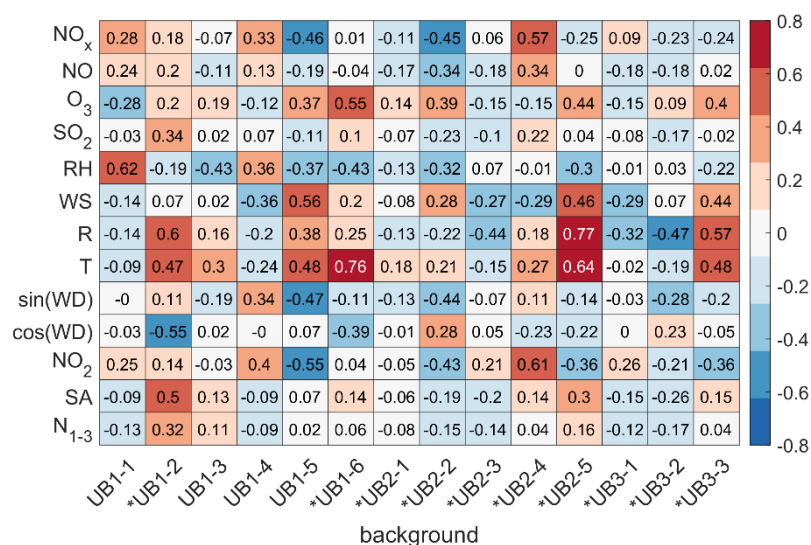
378 Figure S12. Heatmap of Pearson correlation coefficients for time series of factors at the street canyon (SC) and the urban
 379 background stations (UB). Selected factors are marked with *.



380

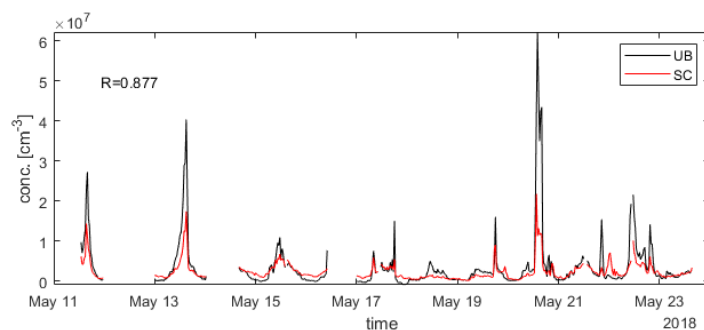
381 Figure S13. Heatmap of Pearson correlation coefficients for time series of factors and other variables at the street canyon
 382 (SC). Selected factors are marked with *. Variables used for correlation analysis consist of concentrations of sulfuric acid
 383 (SA), sub-3 nm particles (N₁₋₃), NO, NO_x, NO₂, O₃, black carbon (BC), carbon oxide (CO), sinus and cosine of wind

384 direction ($\sin(\text{WD})$, $\cos(\text{WD})$), wind speed (WS), temperature (T), relative humidity (RH), and carbon dioxide (CO_2)
 385 (Okuljar et al., 2021).



386

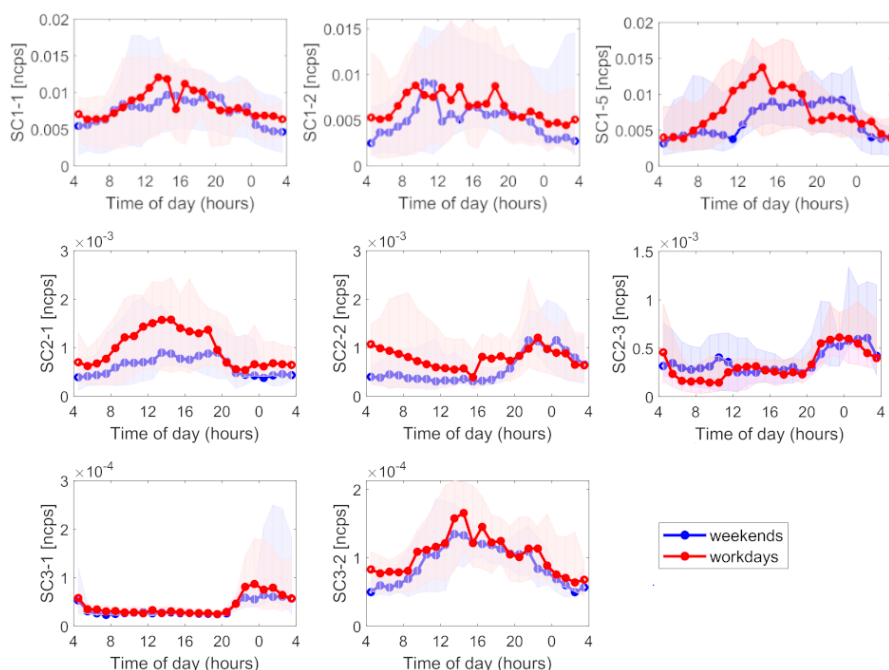
387 Figure S14. Heatmap of Pearson correlation coefficients for time series of factors and meteorological variables at the
 388 urban background station (UB). Selected factors are marked with *. Variables used for correlation analysis consist of
 389 concentrations of NO_x , NO, O_3 , sulfur dioxide (SO_2), relative humidity (RH), wind speed (WS), global radiation (R),
 390 temperature (T), sinus and cosine of wind direction ($\sin(\text{WD})$, $\cos(\text{WD})$), NO_2 , sulfuric acid (SA), sub-3 nm particles
 391 (N_{1-3}) (Okuljar et al., 2021).



392

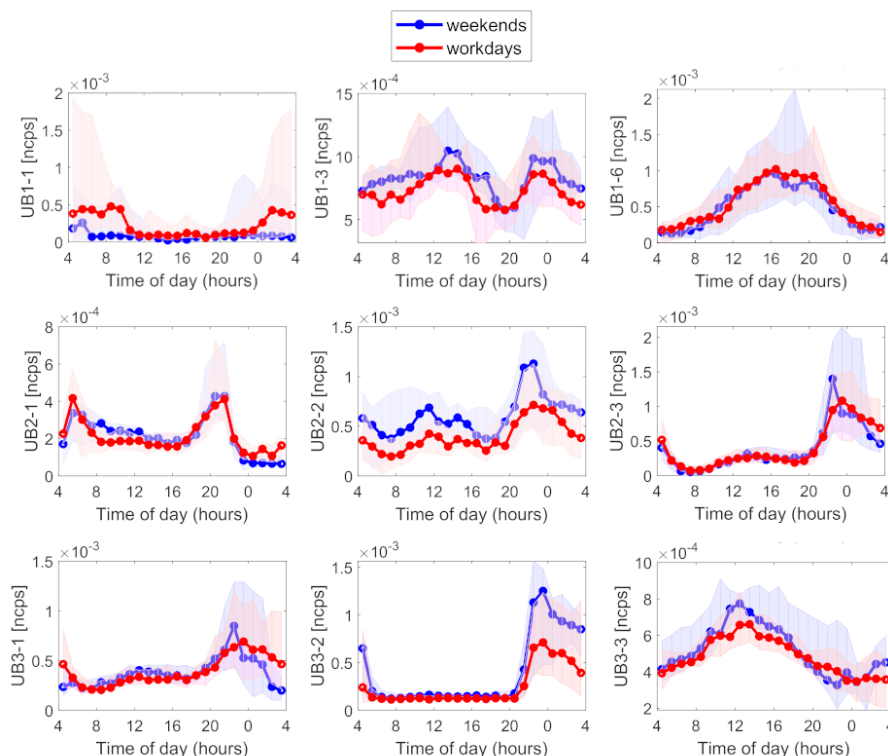
393 Figure S15. Time series of sulfuric acid measured at street canyon (SC)(red) and the urban background station
 394 (UB)(black) for the overlapping time of measurement.

395 **S11. Workday -weekend comparison**



396

397 Figure S16. Examples of the diurnal variation of factors separated in workdays and weekends at the street canyon (SC).
 398 PMF factors are labeled as SCX-Y where X stands for the analyzed m/Q range (1, 2, or 3), and Y is the identifying number
 399 of the factor in that range.



400

401 Figure S17. Examples of the diurnal variation of factors separated in workdays and weekends at the urban background
 402 station (UB). PMF factors are labeled as UBX-Y where X stands for the analyzed m/Q range (1, 2, or 3), and Y is the
 403 identifying number of the factor in that range.

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