1   List of content:

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

12   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
O$_3$	UV-absoption / Teledyne Instruments API 400E	4
SO$_2$ [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/m^2]	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
O$_3$ [µg/m3]	UV fluorescence analyzer / Horiba APOA-370	4
Relative humidity [%]	Vaisala WXT 536	4
Air temperature [°C]	Vaisala WXT 536	4
Wind direction [°]	Vaisala WXT 536	4
Wind speed [m/s]	Vaisala WXT 536	4
Black carbon	Optical analyzer / MAAP 5012	4

13

14 **S2. PMF inputs and validation**

15 **Data preparation**

16 PMF analysis was performed on three different m/Q ranges from UMR data at each station: 200-350 Th, 350-500 Th, and

17 500-650 Th (range 1, 2, and 3). The time resolution of the input data was 30 minutes. At the urban background station,

18 during most of the studied time, we detected water clusters; the impurities formed by clustering water molecules with

19 reagent ions. Their appearance in the ambient sample depends on the settings of CI-API-TOF and the sampled RH. For

20 range 1, water clusters were a weighty fraction of the spectrum, thus they were taken out from the data set before running

21 PMF. We removed data at $188 + n*18$ and $251 + n*18$ Th which correspond to $(HNO_3)_{2-3}(H_2O)_nNO_3^-$ molecules.

22 Additionally, the reagent ion tetramer $(HNO_3)_3NO_3^-$ (251 Th) had a big contribution in the dataset at the urban background

23 site, thus it was removed from the PMF analysis. At the street canyon water clusters and $(HNO_3)_3NO_3^-$ were not detected.

24 **Selecting number of factors**

25 We performed PMF analysis for a 2-7 factor solution for each range at both stations. For each solution, we analyzed a

26 diagnostic parameter Q/Q_{exp} (Canonaco et al., 2013), which for an ideal PMF run without downweighing would decrease

27 to 1. Since we downweighed errors, we do not expect Q/Q_{exp} to equal 1 but rather stabilize. In all cases we observed

28 stabilization of Q/Q_{exp} value; however, this parameter itself was usually not conclusive enough to determine the number

29 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

30 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

31 background station. Factor UB3-3 is the only daytime factor in this range and including it in the solution, clarified results

32 of factors 1 and 2. At the same time including more factors did not bring any new information to the solution. For the rest

33 of the PMF solutions at both sites, we chose a 5- or 6-factor solution. We used time series, diurnal variations, and mass

34 spectral profiles to estimate the relevance of different factor solutions for our study. We looked for spectral features or

35 time behaviors that we could associate with atmospheric processes. Alternatively, we included an additional factor if its

36 characteristics differed from all proceeding factors in that solution. In all cases, the unexplained fraction of the spectrum

37 for chosen solution stays between 9 and 12.1%.
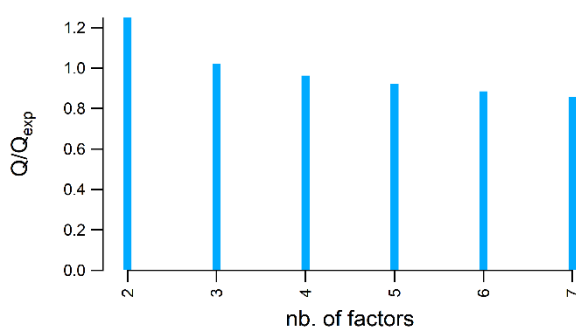
39 Figure S1. Q/Q_{exp} value for 2-7 factors solution for range 3 at street canyon site.

40 **S3. Factor interpretation**

41 In this section, we describe PMF factors and the reasons behind the suggested VOC types, oxidants, terminators, and

42 inhibitors in Tables 1 and S3. As mentioned in section 1, O_3 and NO_3 are selective towards compounds that they react

43 with in the atmosphere, while OH reacts with almost any compound. The chemoselectivity of NO_3 and O_3 towards

44   VOC results in a mass spectrum with a clear pattern, observed before in laboratory experiments (e.g., Ehn et al., 2014;

45   Dam et al., 2022) and ambient measurements (e.g., Yan et al., 2016). At the same time, a mass spectra containing HOM

46   oxidized by OH looks messier, as OH oxidized most VOC in the atmosphere. In the description of factors, we say that

47   we observe chemoselectivity of the oxidant when we notice a pattern in the mass spectrum, and we call the oxidant not

48   chemoselective when there is no pattern in the mass spectrum. We are not able to analyze the influence of HO_2 as a

49   terminator, thus HO_2 could potentially be a terminator for all the factors, except for factors UB3-2 and SC3-1, which

50   must be terminated by RO_2. All key compounds were detected as clusters with NO_3^-, however, for clarity of the

51   interpretation we write their chemical structures in the descriptions without the NO_3^- adduct.

52   •   Street canyon

53   •   Selected factors

54   All factors from range one at street canyon are marked as 'not selected', thus the description of selected factors at street

55   canyon starts with range 2. The timeseries of the SC factors are shown in Figure 3 in the main text, while spectra are

56   presented in Figure S2.

57   **SC2-1, "MT monomers 1"**

58   **Temporal behavior:** SC2-1 factor is a daytime factor reaching maximum concentration at 13:00, suggesting that either

59   OH• or O_3 is the main oxidant.

60   **Spectral features:** The key compounds contain $C_{10}H_{16}O_{8-10}N_{0-2}$ and/or $C_9H_{14,16}O_{9-10}N_2$ (Table S2) suggesting biogenic

61   origin of this factor- MT. The pattern in mass spectrum suggests chemoselectivity of the oxidant towards VOC precursors

62   (Fig. S2), which could imply that the main oxidant is O_3, even though OH could also participate in oxidation reactions.

63   The presence of ONCs suggests that NO is the main terminator.

64   **Other:** SC2-1 correlates with *SC1-1: nitrophenol 1* (R=0.79), *SC1-5: nitrophenol & aliphatic* (R=0.70), *SC3-2:*

65   *photooxidation* (R=0.80) as well as *UB1-2: nitrophenol* (R=0.75), and *UB1-6: C7-8* (R=0.66).

66   **SC2-2, "370+433"**

67   **Temporal behavior:** SC2-2 reaches the highest concentrations during nighttime at 11 p.m., but it is also present during

68   the morning. Diurnal variation suggests NO_3. or O_3 as oxidants.

69   **Spectral features:** SC2-2 is a factor mostly driven by one compound: $C_{10}H_{16}O_9N_2$ (Table S2), which is detected as two

70   separate clusters (370 Th with NO_3^- and 433 Th with $HNO_3NO_3^-$).

71   **Other:** SC2-2 correlates with *SC1-4: unidentified 2* (R=0.62), *UB2-4: MT monomers 3* (R=0.75) as well as CO_2 (R=0.60)

72   and NO_2 (R=0.58). SC2-2 and *B2-4: MT monomers 3* are both factors driven mostly by $C_{10}H_{16}O_9N_2$, however, *UB2-4:*

73   *MT monomers 3* contains also other compounds.

74   **SC2-3, "MT monomers 2"**

75   **Temporal behavior:** SC2-3 reaches the highest concentrations during nighttime, but it is also slightly elevated between

76   11:00 and 16:00. Nighttime behavior suggests that NO_3 is the main oxidant. A morning drop of SC2-3 corresponds to an

77   increase in NO; this indicates that NO may act as an inhibitor for the formation of this factor.

78 **Spectral features:** The key compounds contain $C_{10}H_{16}O_{10-11}N_{0,2}$, which suggests a biogenic origin: MT. The presence of
79 ONCs confirms that NO_3 may be the main oxidant.

80 **Other:** SC2-3 correlates with *SC3-1: MT dimers* (R=0.72) and *UB3-2: MT dimers* (R=0.62), both are factors containing
81 MT dimers. This suggests that SC2-3 could be also terminated by RO_2.

82 **SC3-1, "MT dimers"**

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

86 **Spectral features:** SC3-1 contains $C_{20}H_{32}O_{11-15}N_2$ (Table S2), which are MT dimers. This implies that RO_2 terminates
87 the formation of SC3-1. The presence of ONCs suggests that NO_3 is the dominant oxidant for this factor.

88 **Other:** SC3-1 correlates with *SC2-3: MT monomers 2* (R=0.72) and *UB3-2: MT dimers* (R=0.77).

89 **SC3-2, "photooxidation"**

90 **Temporal behavior:** SC3-2 is a daytime factor reaching maximum at 13:00 when it is responsible for approximately 50%
91 of the measured signal in this range (Fig. S4). Due to diurnal variation, SC3-2 is most likely terminated by NO.

92 **Spectral features:** The mass spectrum of SC3-2 is noisy and without a visible pattern (Fig. S3), thus the oxidant is most
93 likely not chemoselective. That points at OH as the main oxidant. Nevertheless, O_3 could also act as an oxidant. SC3-2
94 contains HOM with 19 or 20 carbons, though identification of many key compounds is hindered by the low S/N ratio.
95 SC3-2 contains HOM, noise, and F-impurities.

96 **Other:** SC3-2 correlates with many other factors at the street canyon. It has the highest correlation with *SC2-1: MT*
97 *monomers 1* (R=0.80) and it also correlates with *UB1-6: C7-8* (R=0.77).

98 - Not selected factors

99

100 The timeseries, spectra and diurnal profiles for "not selected" factors at UB can be found in Figure S6.

101 **SC1-1, "nitrophenol 1"**

102 **Temporal behavior:** SC1-1 is daytime factor with maximum at 13:00. Diurnal variation suggests that OH• or O_3 are
103 oxidants involved in the formation of this factor.

104 **Spectral features:** SC1-1 consists of $C_6H_5O_3N$, $C_7H_7O_3N$, $C_6H_5O_3NHNO_3$, $C_{10}H_{15}O_8N$. The mass spectrum contains
105 mainly nitrophenol, which suggests an anthropogenic origin of SC1-1. SC1-1 includes ONCs, which implies an
106 involvement of NO_x.

107 **Other:** SC1-1 correlates with many factors at street canyon: *SC1-2: MT monomers 3* (R=0.87), *SC2-1: MT monomers 1*
108 (R=0.79), and *SC3-2: photooxidation* (R=0.77) as well as with *UB2-4: MT monomers 3* (R=0.66)

109 **Reason for not "selecting":** SC1-1 has very similar temporal trend to other factors in this range at the street canyon. As
110 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.

SC1-2, "MT monomers 3"

Temporal behavior: SC1-2 is a daytime factor with a maximum at13:00, which suggests that OH or O_3 are involved in the formation of this factor.

Spectral features: SC1-2 contain $C_7H_{10}O_4$, $C_9H_{15}O_6N$, $C_{10}H_{15}O_7N$, $C_{10}H_{17}O_7N$ or $C_{10}H_{15}O_8$, and $C_{10}H_{15}O_8N$, suggesting the biogenic origin of VOCs- MT. SC1-2 often contains ONCs, implying an involvement of NO.

Other: SC1-2 correlates with *SC1-1: nitrophenol 1* (R=0.87), *SC2-1: MT monomers 1* (R=0.79), *SC3-2: photooxidation* (R=0.71), and with *UB1-6: C7-8* (R=0.63). Factor SC1-2 is very similar to SC1-1.

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

SC1-3, "unidentified 1"

Temporal behavior: SC1-3 is a factor elevated from 12:00 to 23:00. That suggests O_3 as the most dominant oxidant.

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

Other: SC1-3 correlates with *SC3-2: photooxidation* (R=0.67) and *UB1-6: C7-8* (R=0.74).

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

SC1-4, "unidentified 2"

Temporal behavior: SC1-4 is a factor elevated during most of the time except between 16:00 and 21:00 (Fig. S6).

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

Other: SC1-4 correlates with *SC2-2: 370+433* (R=0.62), CO_2 (R=0.50).

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

SC1-5, "nitrophenol & aliphatic"

Temporal behavior: SC1-5 is a daytime factor with a maximum at 2 p.m. (Fig. S6), which suggests OH or O_3 as the main oxidant.

Spectral features: SC1-5 contains: $C_6H_5O_3N$, $C_5H_7O_6N$, $C_6H_9O_6N$, $C_6H_{11}O_6N$, $C_7H_{11}O_6N$, $C_7H_9O_7N$ and/or $C_8H_{13}O_6N$, $C_6H_{10}O_8N_2$, $C_7H_{12}O_8N_2$ or $C_8H_{12}O_9$, $C_8H_{12}O_9N_2$ or $C_9H_{14}O_9N$. Key compounds include nitrophenol as well as ions previously detected in China and identified as the product of oxidation of aliphatic VOCs (Guo et al., 2022; Liu et al., 2021), implying that SC1-5 is formed of anthropogenic VOCs. Almost all key compounds are ONCs suggesting an involvement of NO in the formation of SC1-5. There is no clear pattern in a mass spectrum (Fig. S6), suggesting that the main oxidant is not chemoselective: OH.

5

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

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

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

148   **Temporal behavior:** SC2-4 is a daytime factor with a maximum at 14:00 (Fig. S6), which suggests OH or O_3 as the main
149   oxidant.

150   **Spectral features:** Factor SC2-4 has similar time series to factors SC2-1 and SC2-2, which makes it impossible to
151   determine a molecular composition of key compounds. The oxidant is most likely not chemoselective towards VOCs,
152   which suggests OH as the most dominant oxidant (Fig. S6). However, O_3 may also play a role as an oxidant for SC2-4
153   formation.

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

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

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

158   **Temporal behavior:** SC2-5 is a daytime factor with a maximum at 14:00 (Fig. S6), which suggests OH or O_3 as the main
159   oxidant.

160   **Spectral features:** SC2-5 is driven mostly by one peak at 355 Th. The lack of a pattern in the mass spectrum (Fig. S6)
161   indicate an oxidant which is not chemoselective towards VOCs precursors, thus most likely this factor is formed through
162   OH oxidation. O_3 could also partly participate in formation of this factor.

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

164   **Reason for not "selecting":** SC2-5 contains mainly one unidentified peak. Signals of other ions are too small to be
165   determined as key compounds of this factor (Fig. S6).

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

167   **Temporal behavior:** SC3-3 has no clear pattern in time series or diurnal variation (Fig. S6).

168   **Spectral features:** Mass spectrum shows only noise (Fig. S6).

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

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

172   •   Urban background station

173   •   Selected factors

174   The timeseries of the UB factors are shown in Figure 4 in the main text, while spectra are presented in Figure S3.

UB1-2, "nitrophenol"

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

Spectral features: UB1-2 contains mainly C4-10 compounds. The double bound equivalent (DBE) between 2 and 6 of key compounds indicates that some of them may have an aromatic ring (Table S2). UB1-2 includes nitrophenol ($C_6H_5O_3N$), known as a biomass burning combustion tracer as well as a compound formed from benzene and phenol oxidation, which are AVOCs. This suggests that compounds in UB1-2 were formed from AVOCs. There is no clear pattern in the mass spectrum (Fig. S3), which may indicate that the oxidant does not show chemoselectivity towards the type of VOC precursors. This combined with the information from diurnal variation suggests the involvement of OH in oxidation reactions. UB1-2 often contains N, suggesting the participation of NO_x in the termination reaction.

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

UB1-6, "C7-8"

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

Spectral features: UB1-6 contains C7-8 compounds, which were previously reported from MT oxidation with non-zero NO_x concentration (Pullinen et al., 2020; Yan et al., 2020) and in ambient measurement (Liu et al., 2021). At the same time, these compounds were found as HOM formed from aromatic VOCs (Guo et al., 2022). A pattern in the mass spectrum (Fig. S3) suggests chemoselectivity of the oxidant towards VOC precursors implying that O_3 may be the dominant oxidant. UB1-6 contains ONCs, which suggests an involvement of NO.

Other: UB1-6 correlates with three factors at street canyon: *SC1-3: unidentified 1* (R=0.74), *SC2-1: MT monomers 1* (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 oxidation mechanism. UB1-6 also correlates with temperature (R=0.76) and O_3 concentration (R=0.55) suggesting O_3 as the main oxidant.

UB2-1, "MT monomers 1"

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

Spectral features: Key compounds contain $C_{9-10}H_{14,16-17}O_{9,11-12}N_{1-3}$ (Table S2), which suggests MT as initial VOCs. UB2-1 contains N, which suggests an involvement of one or both reagents leading to ONCs: NO and NO_3.

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

UB2-2, "MT monomers 2"

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

Spectral features: Key compounds of UB2-2 contain $C_{9-10}H_{14-15,17}O_{9-11}N_{1-3}$ (Table S2), which indicates that this factor is formed from biogenic VOCs - MT. Since all key compounds are ONCs and NO rather acts as an inhibitor, not terminator, UB2-2 is mostly likely oxidized by NO_3. However, we cannot exclude some participation from O_3 in oxidation.

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 dimers* contain MT dimers, UB2-2 could be also terminated by RO_2. UB2-2 has a negative correlation with NO_x (R= -0.45) suggesting that NO is not participating in termination reactions.

UB2-3, "sesquiterpene 1"

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 oxidant and UB2-3 is formed during the absence of NO.

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

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

UB2-4, "MT monomers 3"

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

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 Th). The key compounds contain $C_{9-10}H_{14,16}O_{9-11}N_{0-2}$ (Table S2), which suggests the biogenic origin of the VOC precursors – MT.

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

UB2-5, "photooxidation 1"

Temporal behavior: UB2-5 is a daytime factor with a maximum at 12:00 (Fig. 4), at that time it corresponds to more than 50% of the signal at this range (Fig. S5). The diurnal variation suggests that UB2-5 is oxidized mainly by OH.

Spectral features: The mass spectrum of UB2-5 has no clear pattern in it, which suggests OH as the main oxidant (Fig. S3). 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 $C_{10}H_{16}O_9N_2$ (Table S2). The presence of ONCs suggests that HOM in UB2-5 are terminated by NO. UB2-5 most likely contains VOCs oxidized by OH and a noise. We cannot exclude O_3 as an oxidant for this factor.

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

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

245 **Temporal behavior:** UB3-1 is a nighttime factor with a maximum at 11:00 (Fig. 4). The highest concentrations of UB3-
246 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,
247 OH is not involved in the oxidation.

248 **Spectral features:** Key compounds contain $C_{15}H_{24-25}O_{13-16}N_{1-2}$ (Table S2), which suggests a biogenic origin of VOCs,
249 likely sesquiterpenes based on the number of C and H. The presence of ONC implies that UB3-1 is formed by NO_3
250 oxidation, however, we cannot exclude O_3 as an oxidant.

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

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

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

256 **Spectral features:** UB3-2 contains as key compounds dimers of MT: $C_{17-18}H_{26}O_{14-16}N_{0-2}$, $C_{20}H_{30-32}O_{13-16}N_{0-2}$, and possibly
257 $C_{19}H_{30}O_{13}N_2$ (Table S2). Since UB3-2 contains dimers, the formation of this factor must be terminated by RO_2. The
258 presence of ONC implies that NO_3 is the main oxidant, however, O_3 could also be involved in oxidation reactions.

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

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

261 **Temporal behavior:** UB3-3 is a daytime factor with a maximum at 12:00, which represents 60% of the measured signal
262 at this range during morning and noon (Fig. S5). The diurnal variation suggests that UB3-1 is oxidized mainly by OH.

263 **Spectral features:** The mass spectrum of UB3-3 is noisy and does not show any pattern (Fig. S3), implying not
264 chemoselective main oxidant: OH. The only compounds identified in this factor were F-impurities. Since UB3-3
265 sometimes contains more than 50% of the measured signal, we suspect that it also contains HOM which we cannot identify
266 due to the low S/N ratio.

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

268 • Not selected factors

269 The timeseries, spectra and diurnal profiles for "not selected" factors at UB can be found in Figure S7.

270 **UB1-1, "Water clusters"**

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

274 **Spectral features:** The mass spectrum of factor UB1-1 contains mostly m/Q 1 and 2 Th higher than m/Q of removed
275 water clusters (Fig. S7). Key compounds of that spectrum were identified as isotopes of water clusters.

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

277 **Reason for not "selecting":** UB1-1 contains only isotopes of water clusters, an artefact.

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

279 **Temporal behavior:** UB1-3 has two maxima: daytime at 13:00 and nighttime at 23:00 (Fig. S7), suggesting that
280 atmospheric condition at the station does not drive that factor.

281 **Spectral features:** UB1-3 is never a dominant factor during the campaign and its key compounds correspond to key
282 compounds of other factors from this range; thus, the only key compound identified is $C_9H_{14}O_8N_2$. It is likely that either
283 NO, NO_3, or both are involved in the formation of UB1-3. We cannot identify which oxidant participates in the formation
284 of that factor. However, the lack of a pattern in mass spectrum may indicate that the oxidant is not chemoselective towards
285 VOC precursors (Fig. S7). This makes O_3 the less likely oxidant to participate in the formation of B1-3.

286 **Other:** UB1-3 correlates with *UB2-2: MT monomers 1* (R=0.61) and *SC1-2: MT monomers 3* (R=0.61).

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

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

291 **Temporal behavior:** UB1-4 has a maximum at 5:00 and it reaches the lowest concentrations between 8:00 and 13:00
292 (Fig. S7). The diurnal variation suggests that NO does not participate in the termination reaction of that factor.

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

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

296 **Reason for not "selecting":** We are not able to undoubtfully identify any compound in UB1-4.

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

298 **Temporal behavior:** UB1-5 is a daytime factor elevated between 10:00 and 16:00 (Fig. S7). That suggests an
299 involvement of O_3 or OH in the oxidation. Diurnal variation of B1-5 shows higher concentrations when NO is present at
300 the background station (Fig. S7 and Fig. 2).

301 **Spectral features:** UB1-5 is a daytime factor with a mass spectrum mostly driven by one m/Q (261 Th, Fig. S7), which
302 cannot be identified. The only compound which we can certainly identify is $C_{10}H_{16}O_8N$ (339 Th). The mass spectrum
303 contains several more pronounced peaks with odd m/Q which could be radicals, or due to the nitrogen rule, ONC with an
304 odd number of nitrogen molecules. HOM in UB1-5 may be terminated by NO or HO_2, but NO is presumably the one
305 terminator more involved in the HOM formation. There is no clear pattern in the mass spectrum (Fig. S7), which may

306 indicate that the oxidant is not chemoselective towards VOC precursors. This suggests OH as more likely oxidant than
307 O_3.

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

309 **Reason for not "selecting":** We are not able to undoubtfully identify most of the key compounds in UB1-5.

310 **S4. Chemical composition of selected factors**

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

Range [Th]	Factor	Composition
	Street canyon	
350-500	SC2-1: MT monomers 1	354: $C_{10}H_{16}O_8N_2NO_3$-
		356: $C_9H_{14}O_9N_2NO_3$- or/and $C_{10}H_{16}O_9NNO_3$-
		358: $C_9H_{16}O_9N_2NO_3$- or/and $C_{10}H_{16}O_{10}NO_3$-
		370: $C_{10}H_{16}O_9N_2NO_3$-
		372: $C_{10}H_{16}O_{10}NNO_3$- or/and $C_9H_{14}O_{10}N_2NO_3$-
	SC2-2: 370+433	370: $C_{10}H_{16}O_9N_2NO_3$-
		433: $C_{10}H_{16}O_9N_2NO_3HNO_3$-
	SC2-3: MT monomers 2	358- $C_{10}H_{16}O_{10}NO_3$-
		386- $C_{10}H_{16}O_{10}N_2NO_3$-
		402- $C_{10}H_{16}O_{11}N_2NO_3$-
500-650	SC3-1: MT dimers	538: $C_{20}H_{32}O_{11}N_2NO_3$-
		554: $C_{20}H_{32}O_{12}N_2NO_3$-
		570: $C_{20}H_{32}O_{13}N_2NO_3$-
		586: $C_{20}H_{32}O_{14}N_2NO_3$-
		602: $C_{20}H_{32}O_{15}N_2NO_3$-
	SC3-2: photooxidation	500: $C_{19}H_{22}O_{10}N_2NO_3$-
		502: $C_{19}H_{24}O_{10}N_2NO_3$-
		508: $C_9F_{16}H_2O_2NO_3$-
		558: $C_{10}F_{18}H_2O_2NO_3$-
	Urban background station	
200-350	UB1-2: nitrophenol	201: $C_6H_5O_3NNO_3$-
		217: $C_6H_5O_4NNO_3$-
		234: $C_7H_8O_5NO_3$-
		241: $C_4H_5O_7NNO_3$-
		288: $C_{10}H_{10}O_6NO_3$- or $C_6H_{10}O_9NO_3$-
	UB1-6: C7-8	250: $C_8H_{12}O_5NO_3$-
		297: $C_7H_9O_8NNO_3$-
		313: $C_8H_{13}O_8NNO_3$- or $C_8H_{12}O_5\ HNO_3NO_3$-
350-500	UB2-1: MT monomers 1	356: $C_9H_{14}O_9N_2NO_3$- or $C_{10}H_{16}O_9NNO_3$-
		388: $C_{10}H_{16}O_{11}NNO_3$- or $C_9H_{14}O_{11}N_2NO_3$-
		433: $C_{10}H_{17}O_{12}N_3NO_3$-
	UB2-2: MT monomers 2	355: $C_{10}H_{15}O_9NNO_3$-
		357: $C_9H_{15}O_9N_2NO_3$- or $C_{10}H_{17}O_9NNO_3$-
		371: $C_{10}H_{15}O_{10}NNO_3$-
		372: $C_9H_{14}O_{10}N_2NO_3$-
		387: $C_{10}H_{15}O_{11}NNO_3$-
		403: $C_9H_{15}O_{11}N_3NO_3$-
	B2-3: sesquiterpene 1	407: $C_{15}H_{23}O_8NNO_3$-
		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: $C_{10}H_{16}O_9NNO_3$- or $C_9H_{14}O_9N_2NO_3$-
		358: $C_{10}H_{16}O_{10}NO_3$-

|		
		370: $C_{10}H_{16}O_9N_2NO_3^-$
		372: $C_9H_{14}O_{10}N_2NO_3^-$
		388: $C_{10}H_{16}O_{11}NNO_3^-$
		433: $C_{10}H_{16}O_9N_2NO_3HNO_3^-$
	UB2-5: photooxidation 1	351: $C_{10}H_{11}O_9NNO_3^-$
		370: $C_{10}H_{16}O_9N_2NO_3^-$
500-650	UB3-1: sesquiterpene 2	502: $C_{15}H_{24}O_{13}N_2NO_3^-$ or $C_{15}H_{23}O_{10}NHNO_3NO_3^-$
		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: $C_{11}F_{20}H_2O_2NO_3^-$

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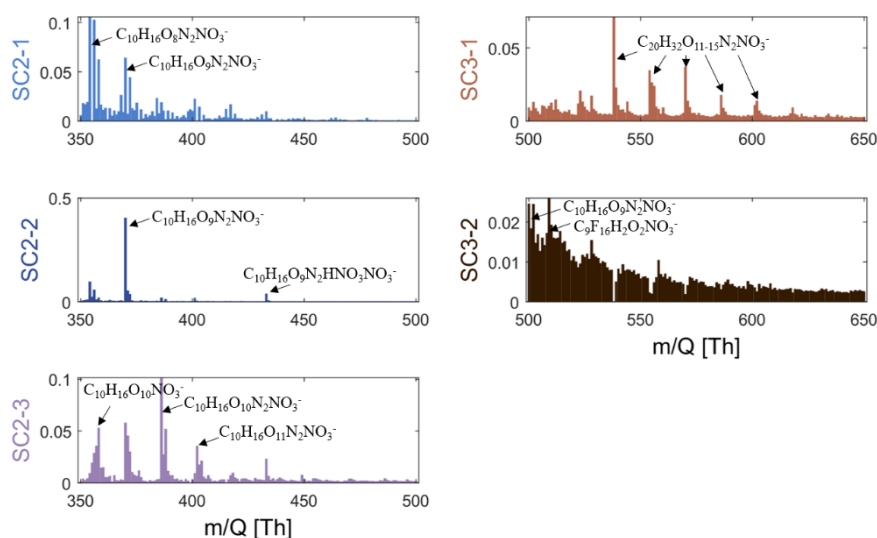
Figure S2. Mass spectra of selected PMF factors at the street canyon (SC). The left panel contains mass spectra for range 350-500 Th, and the right one for 500-650 Th.

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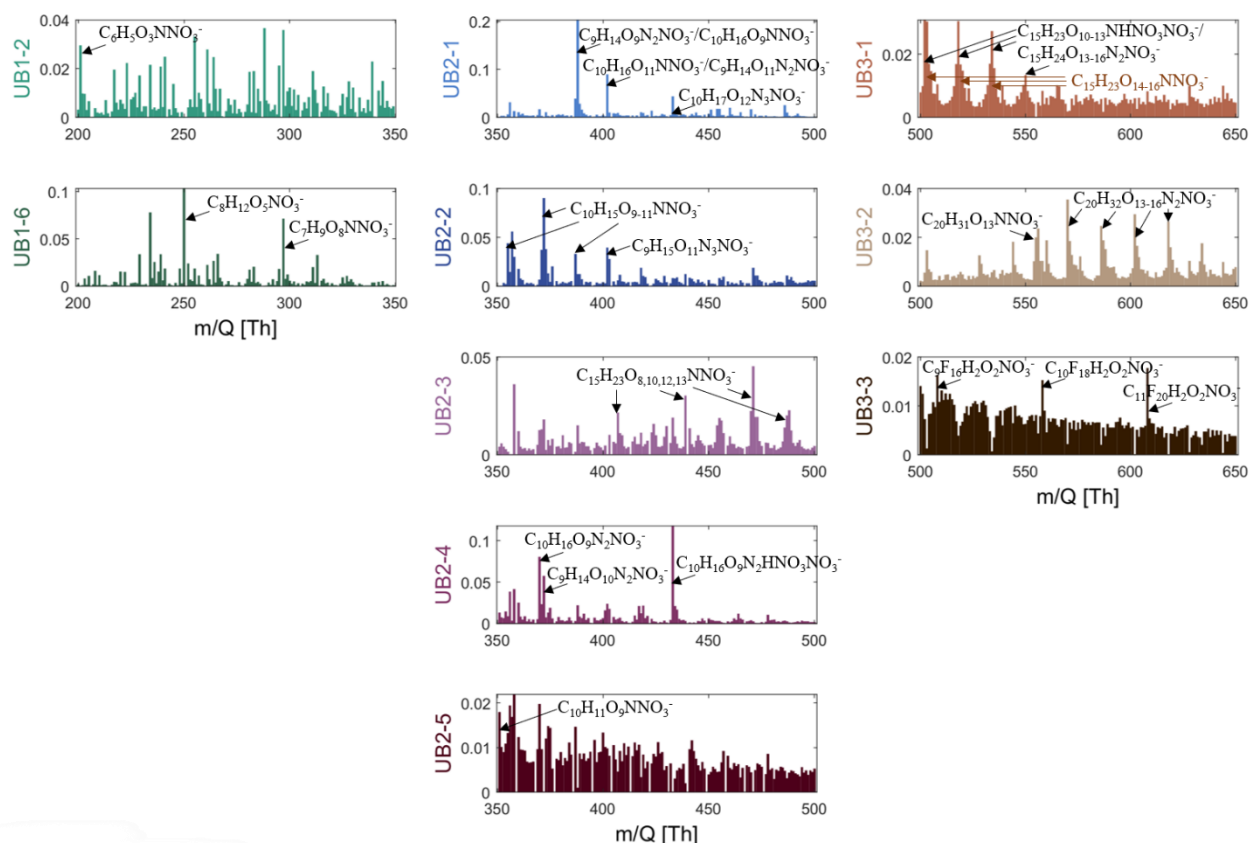
Figure S3. Mass spectra of selected PMF factors at the urban background station (UB). Left panel contains mass spectra for range 200-350 Th, middle one for 350-500 Th, and the right one for 500-650 Th.

S5. Ion fractions of selected factors
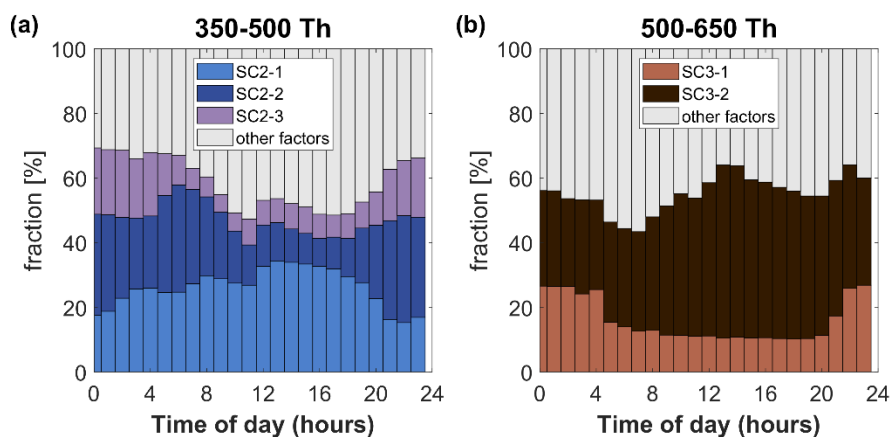
Figure S4. Diurnal variation of the selected factor fractions at street canyon (SC). The left panel contains variation for range 350-500 Th, and the right one for 500-650 Th.
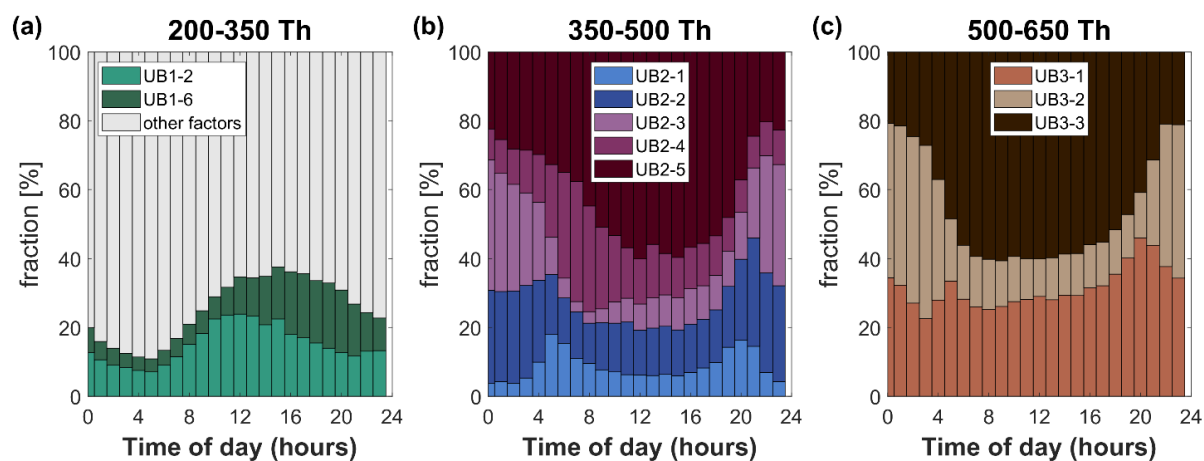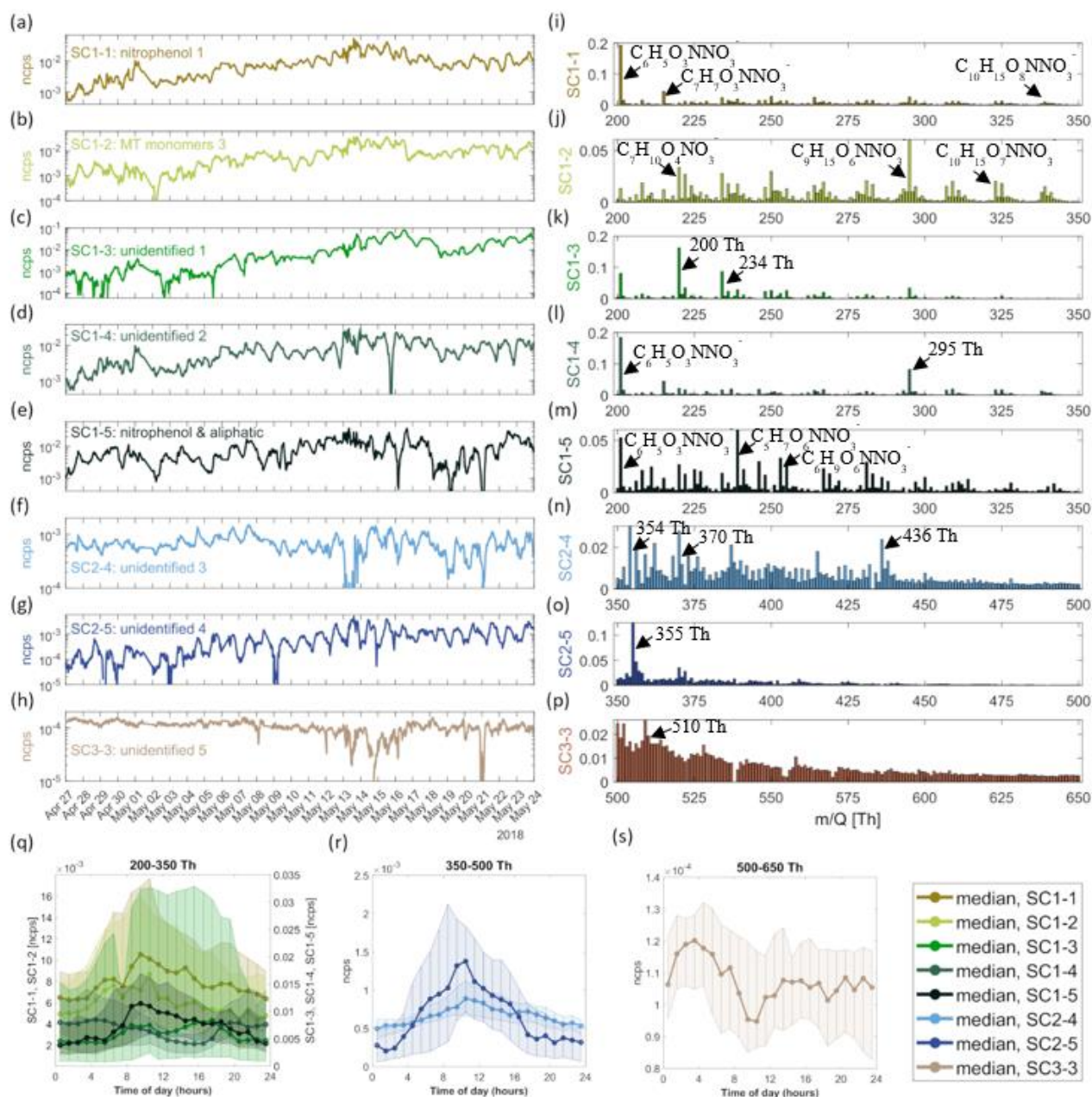
Figure S5. Diurnal variation of the selected factor fractions at urban background station (UB). The left panel contains variation for range 200-350 Th, middle one for 350-500 Th, and the right one for 500-650 Th.
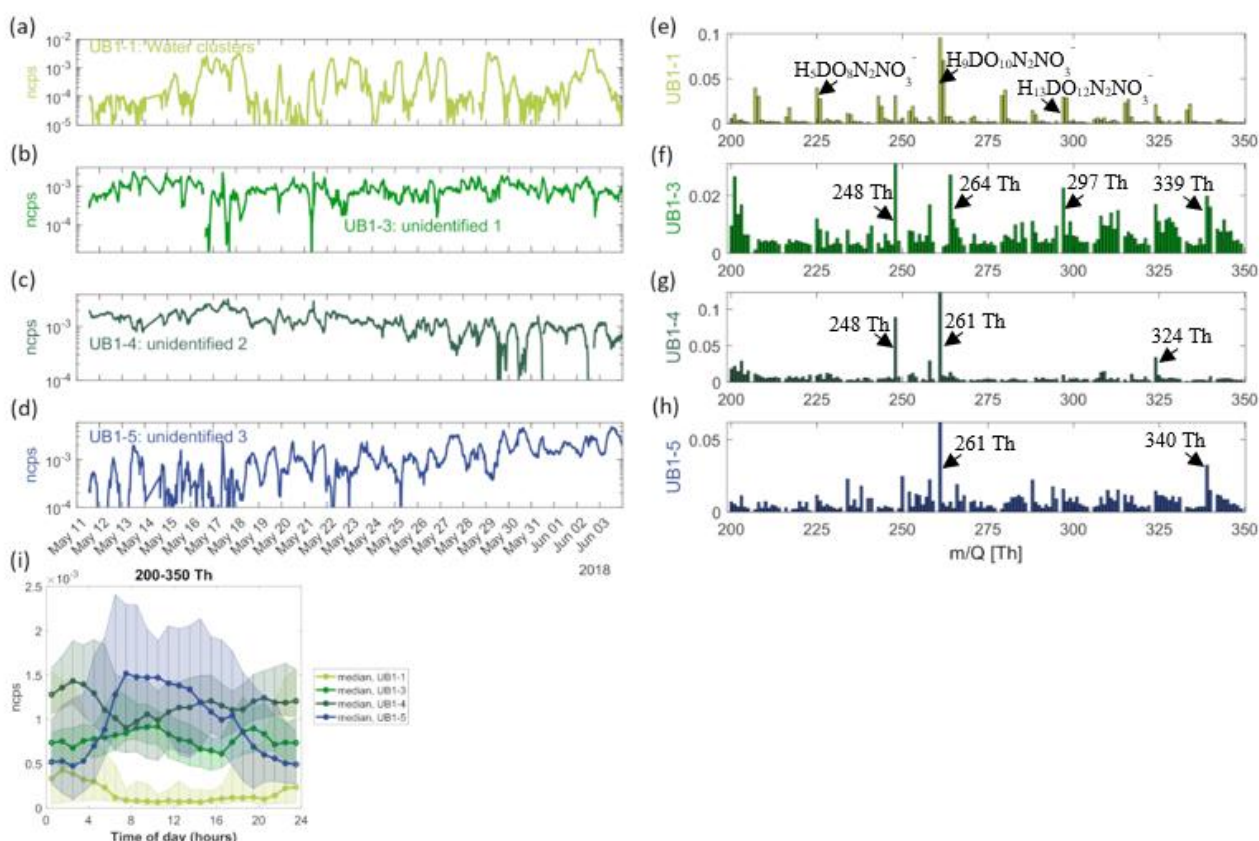
S6. Overview of not selected factors

328

329 Figure S6. Time series of not selected PMF factors (a-h), their mass spectra (i-p), and diurnal variation (q-s) at the street

330 canyon (SC). The median diurnal variation is shown as a solid line with markers; the 25th and 75th percentile ranges are

331 presented as shaded areas.

332

Figure S7. Time series of not selected PMF factors (a-d), their mass spectra (e-h), and their diurnal variation (i) at the urban background station (UB). The median diurnal variation is shown as a solid line with markers; the 25th and 75th percentile ranges are presented as shaded areas.

Table S3. Suggested characterization of not selected factors at both stations. The table contains information about probable precursors, oxidants, terminators of formation mechanisms for HOM as well as information about diurnal variation profile (daytime (D) and nighttime (N)), fraction percentage (%) and potential inhibitors for factors. The 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	NO₃	O₃	NO	RO₂	HO₂		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											
	UB1-1	Water clusters	-	-	-	-	-	-	1	5.3	9.2
200-350	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

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| UB1-5 | VOCs | yes | no | M | yes | no | M | 7 | 12.5 | 21.3 |

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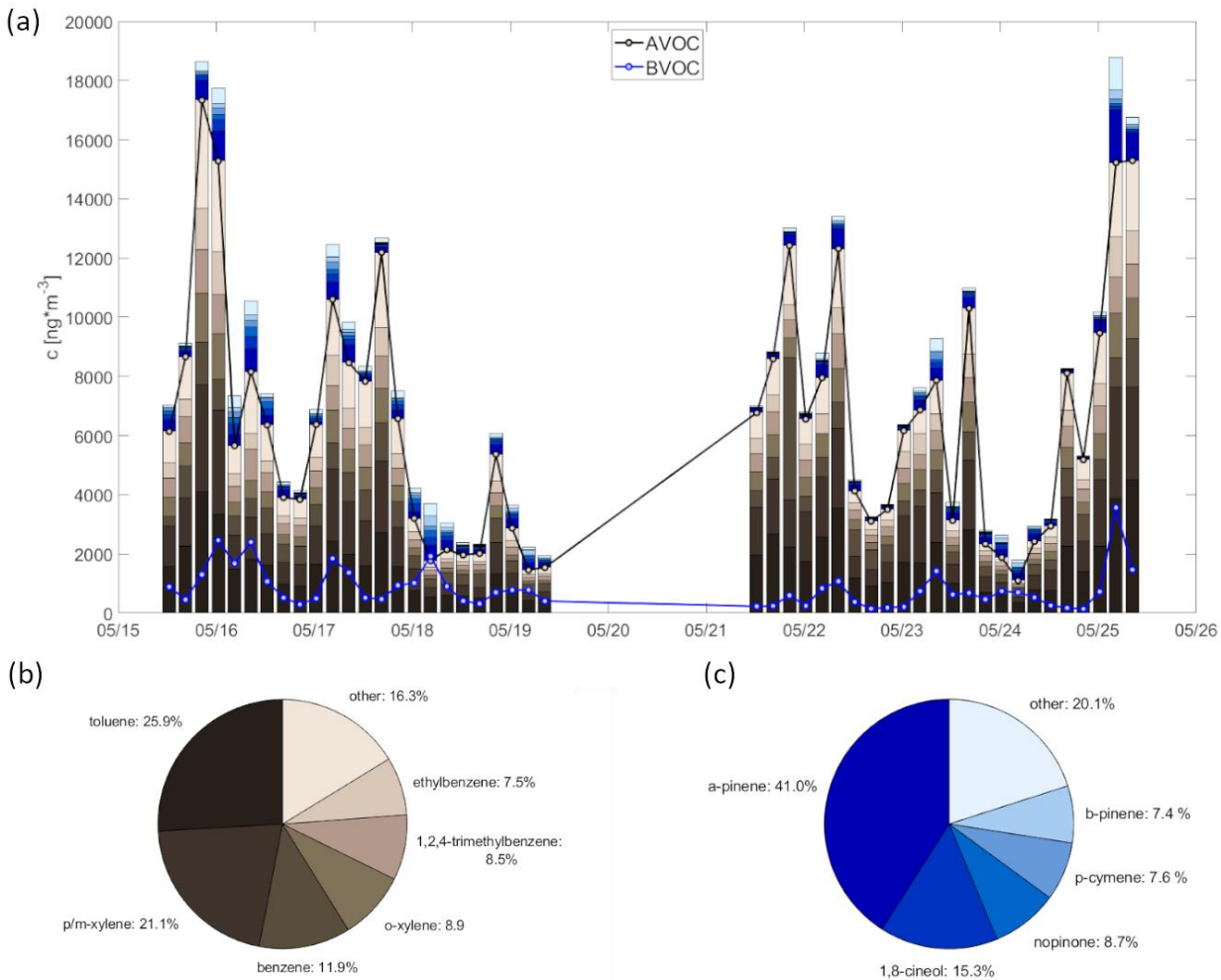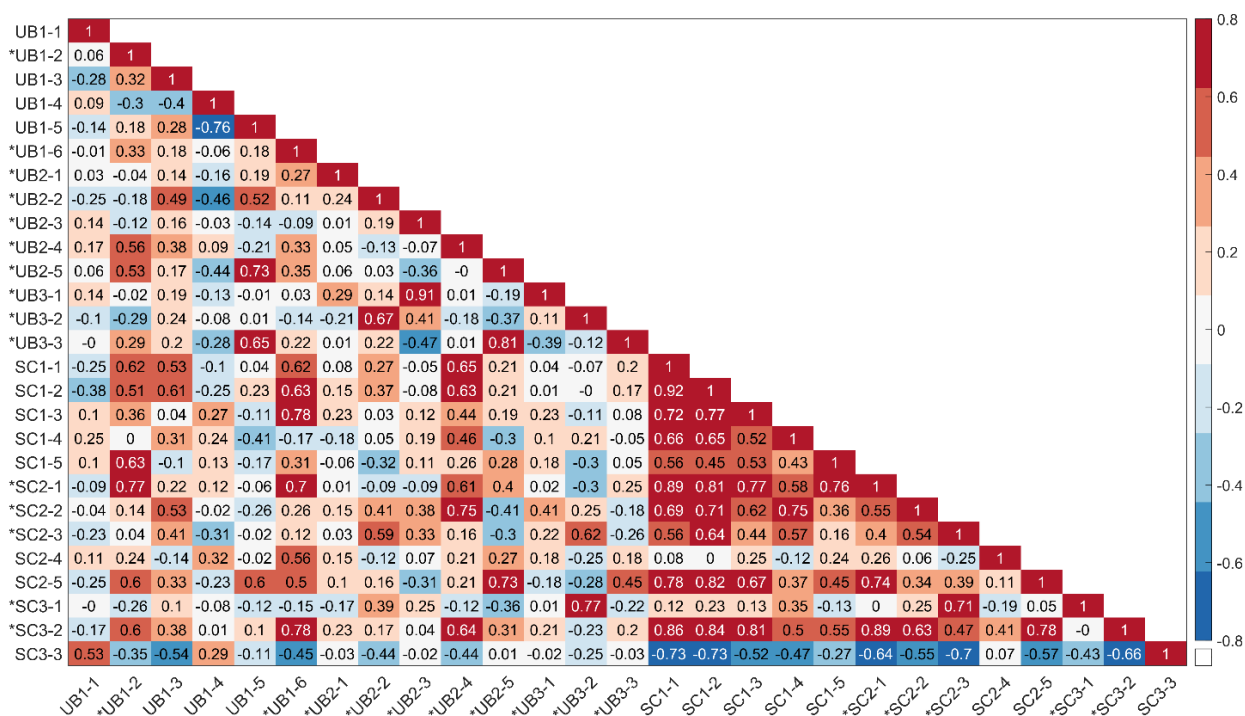**S7. Overview of the measured VOCs at the street canyon**

342

Figure S8. Time series of measured VOCs concentrations (a) and the fraction of an individual AVOC (b) and BVOC (c) at street canyon. BVOCs and AVOCs which do not make more than 5% of corresponding total BVOC and total AVOC concentrations are group as "others".
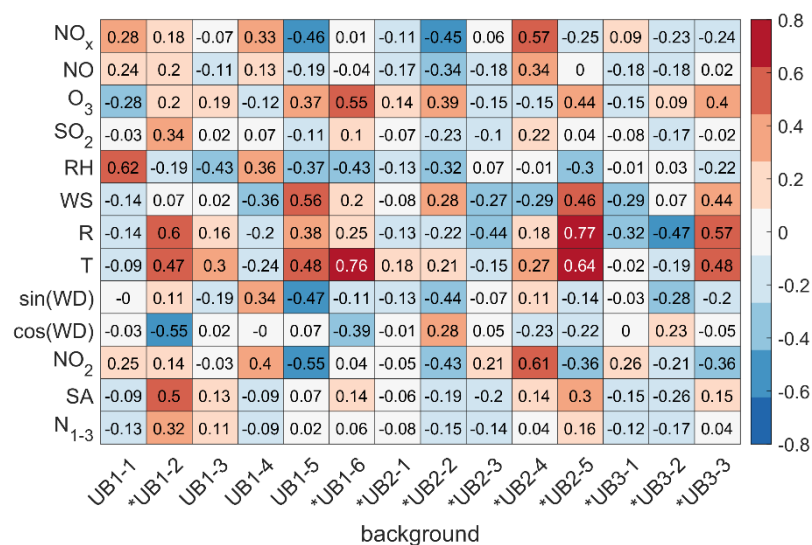
S8. Correlations of observed factors

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Figure S9. Heatmap of Pearson correlation coefficients for time series of factors at the street canyon (SC) and the urban background stations (UB). Selected factors are marked with *.

351
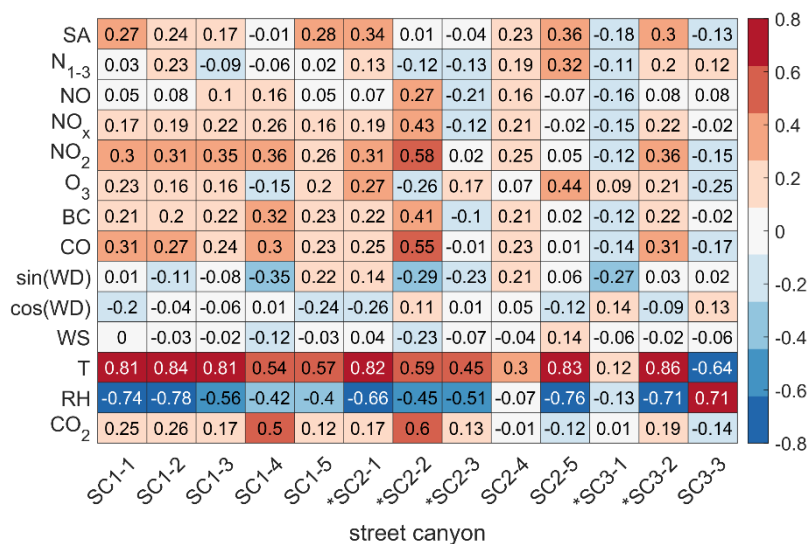
Figure S10. Heatmap of Pearson correlation coefficients for time series of factors and other variables at the street canyon (SC). Selected factors are marked with *. Variables used for correlation analysis consist of concentrations of sulfuric acid (SA), sub-3 nm particles (N_{1-3}), NO, NO_x, NO_2, O_3, black carbon (BC), carbon oxide (CO), sinus and cosine of wind direction (sin(WD), cos(WD)), wind speed (WS), temperature (T), relative humidity (RH), and carbon dioxide (CO_2) (Okuljar et al., 2021).

357

358 Figure S11. Heatmap of Pearson correlation coefficients for time series of factors and meteorological variables at the

359 urban background station (UB). Selected factors are marked with *. Variables used for correlation analysis consist of

360 concentrations of NO_x, NO, O_3, sulfur dioxide (SO_2), relative humidity (RH), wind speed (WS), global radiation (R),

361 temperature (T), sinus and cosine of wind direction (sin(WD), cos(WD)), NO_2, sulfuric acid (SA), sub-3 nm particles (N_{1-}

362 $_3$) (Okuljar et al., 2021).

363 **S9. Workday -weekend comparison**
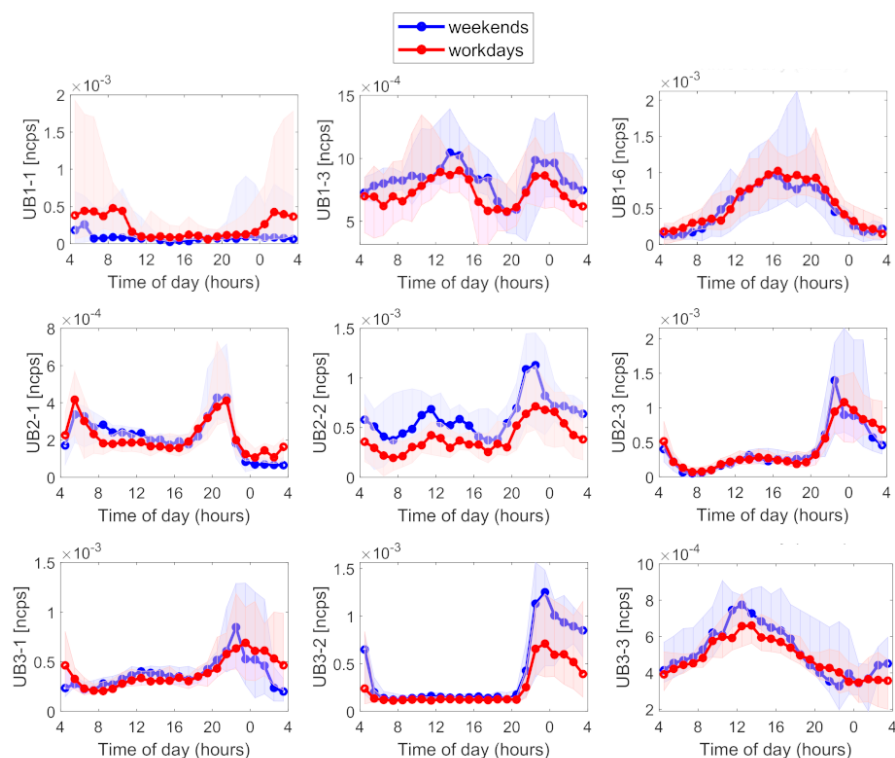
364

365 Figure S13. Examples of the diurnal variation of factors separated in workdays and weekends at the urban background

366 station (UB).

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