

Supplementary Information

Toluene morning peaks as likely indicators of Mediterranean forest stress

Ana M. Yáñez-Serrano^{1,2,3}, Mirto Lampadariou^{1,4}, Iolanda Filella^{2,3}, Joan Llusà^{2,3}, Roger Seco¹, Marcos Fernández-Martínez^{2,3}, Miguel Portillo-Estrada⁵, Ivan A. Janssens⁵, N. Mihalopoulos⁴, Jordi Massagué^{1,6}, Noemi Perez¹, Marjan Savadkoohi^{1,7}, Marco Pandolfi¹, Josep Peñuelas^{2,3}, Xavier Querol¹, Andrés Alastuey¹

[1] Institute of Environmental Assessment and Water Research, IDAEA-CSIC, Barcelona 08034, Spain

[2] CREAM, E08193 Bellaterra (Cerdanyola del Vallès), Catalonia, Spain

[3] CSIC, Global Ecology Unit, CREAM-CSIC-UAB, E08193 Bellaterra (Cerdanyola del Vallès), Catalonia, Spain

[4] University of Crete 70013, Greece

[5] PLECO (Plants and Ecosystems), Department of Biology, University of Antwerp, Wilrijk, Belgium.

[6] Barcelona Supercomputing Center (BSC), Barcelona, Spain

[7] TECNALIA Research & Innovation, Basque Research and Technology Alliance (BRTA), Derio, Spain

1. Methods

a. Location of the MSY station

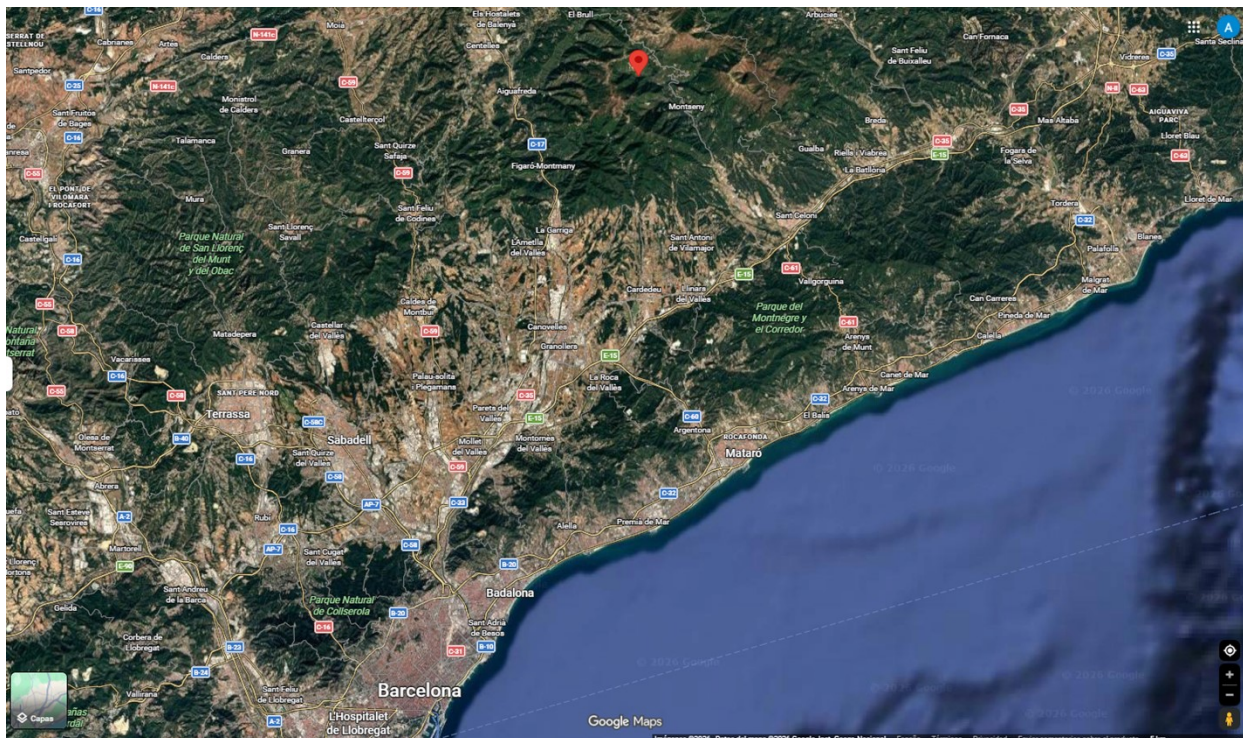


Figure S.1. Map of the region containing the location of the MSY station (red pin) together with the major highways, cities and towns nearby. The image has been obtained from Google Maps.

b. PTR-MS

Table S.1. Table with the limit of detection (LOD), in ppbv, for all the reported compounds during 2021, 2022 and 2023, respectively. Please note this is the LOD for all the year period, not only the summer months.

Compound	2021	2022	2023
Methanol	0.84	1.33	1.16
Acetonitrile	0.03	0.08	0.04
Acetaldehyde	0.18	0.25	0.22
Acetone	0.06	0.11	0.07
Isoprene	0.06	0.24	0.11
MVK+MACR	0.04	0.09	0.07
MEK	0.004	0.11	0.07
Benzene	0.03	0.04	0.04
Toluene	0.06	0.12	0.08
Styrene	0.70	0.11	0.04
Xylenes	0.14	0.38	0.12
Monoterpenes	0.04	0.11	0.05

2. The whole time series of toluene mixing ratios for the monitored period.

In figure S.1. the time series of the whole monitored period from 1st June 2021 to 31st of August 2023 are depicted. Data are separated by summer seasons. Although data were available for the entire year from 2021 to 2023, only summer data (June–August) were analyzed and displayed, as the most pronounced toluene peaks were consistently observed during this period.

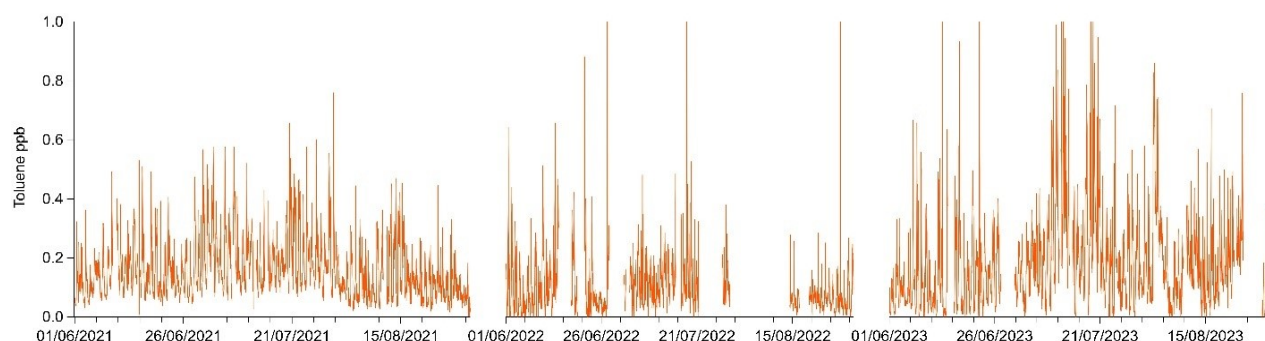


Figure S.2.1: Time series of Toluene mixing ratios (ppbv) measured from June 2021 to August 2023.

Among such period, there were in total 276 days to take into consideration. Out of those, 52 days we had instrument malfunction, so 18.5% of such days have no data. Out of the remaining days, 152 days showed no peak, and 72 days showed a toluene early morning peak. Out of the 72 days with peaks 10 periods were back-to-back periods. Furthermore, out of the 276 days, 143 were considered heat waves. This classification was done when the average daily temperature was above 22°C (including day and night) during more than 3 consecutive days. Out of the 143 days with heatwaves 57 days displayed an early morning toluene peak, however this was also dependent on data availability, as not all heatwaves days there was PTR-MS data available.

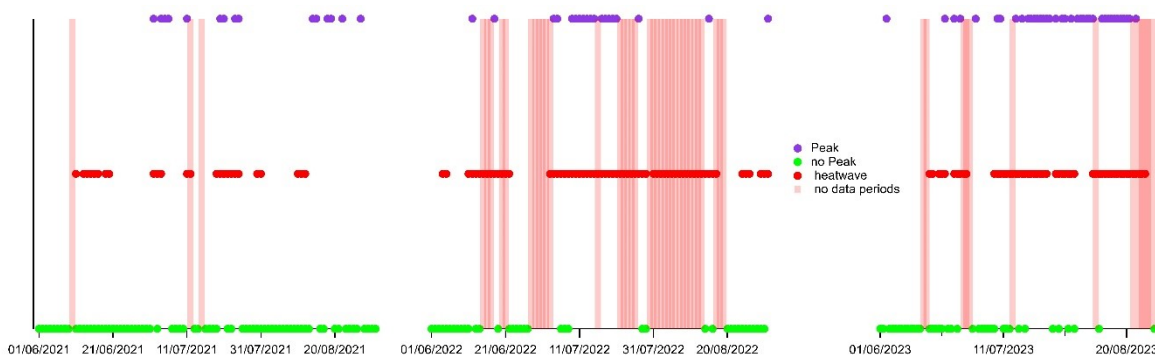


Figure S.2.2.: Data availability during the period of measurements. In green are the periods where the data showed no early morning toluene peak, in purple the days where the peak was available, in red the periods where heat

waves were present (average daily temperature was above 22°C (including day and night) during more than 3 consecutive days). The red bars represent the periods where data was unavailable.

While analyzing the monitored VOC mixing ratio data by the PTR-MS during the summer periods of 2021, 2022 and 2023 we focus on toluene (Figure S.1). A distinct diel cycle of toluene was observed throughout these summer periods (Fig. 2 in the main text). The mixing ratios start to increase early in the morning, from approximately 07:00 local time (LT), and reach their maximum between 12:00 and 15:00 (LT). This daily pattern is consistent across all three years examined. This sharp midday increase is likely associated with the transport of pollutants from the Barcelona urban and industrial area, resulting from enhanced boundary-layer mixing and the onset of the sea breeze effect, combined with emissions from vehicular traffic and industrial sources. After reaching peak values, the mixing ratios remain relatively stable for a few hours before showing a transient increase at 20:30 (LT) to rapidly decline after sunset, around 21:30 (LT)

3. Toluene early morning peak examples

Figure S.2.1 and S.2.2 present two clear examples of early morning toluene peaks observed at the Montseny (MSY) site. On both 23 June 2023 and 18 July 2022, a pronounced and sharp increase in the toluene mixing ratio was recorded during the early morning hours (between 06:00 and 10:00 LT), reaching values up to 1.6 ppbv. Following these peaks, toluene mixing ratios gradually decline, stabilizing at lower levels (~ 0.2-0.4 ppbv) throughout the rest of the day. These recurrent early morning peaks are potentially linked to plant physiological responses under stress conditions, combined with low atmospheric mixing and limited dispersion during early morning hours. Their consistent appearance supports the hypothesis that biogenic emissions, particularly under stress conditions, may significantly contribute to ambient toluene levels during summer mornings.

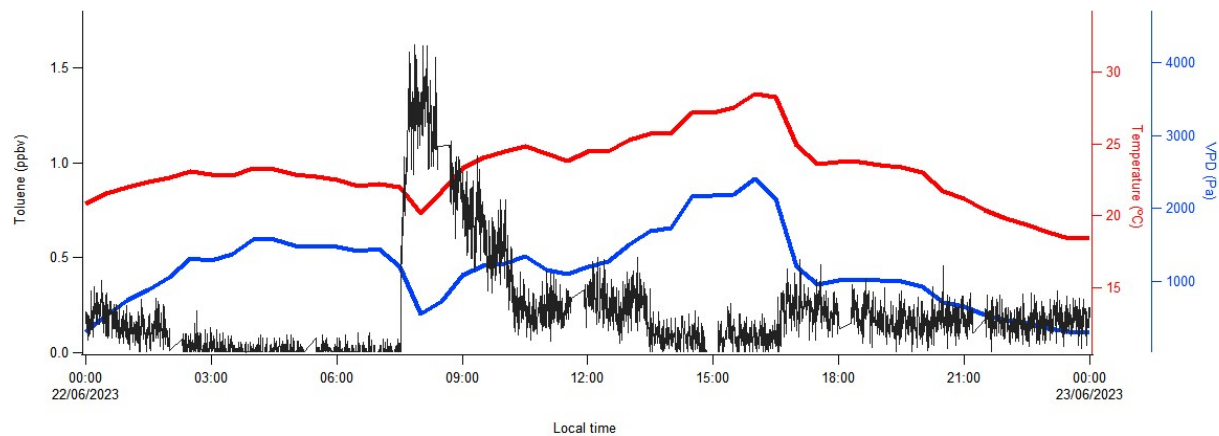


Figure S.3.1.: Toluene mixing ratios (ppbv) for 22 June 2023.

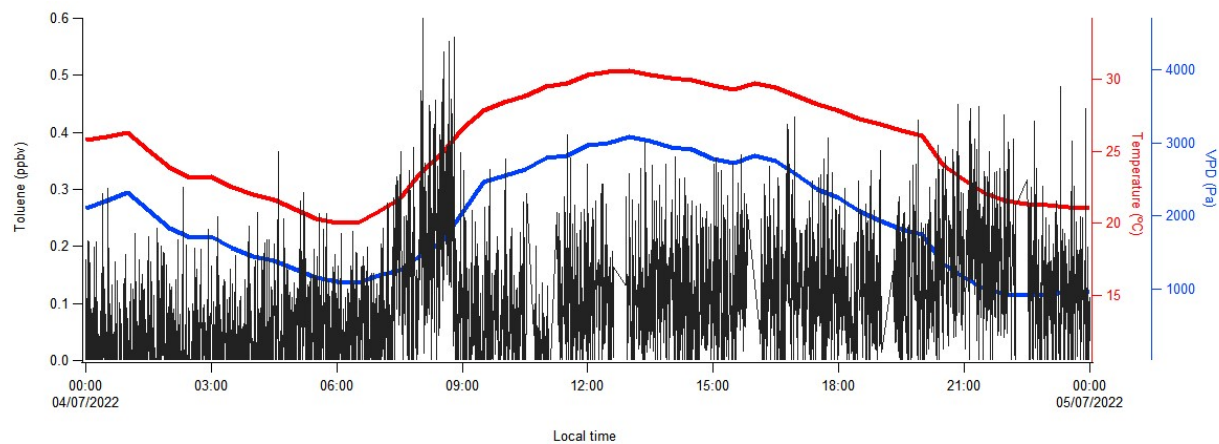


Figure S.3.2.: Toluene mixing ratios (ppbv) for 4 July 2022.

4. Box plots of all available parameters

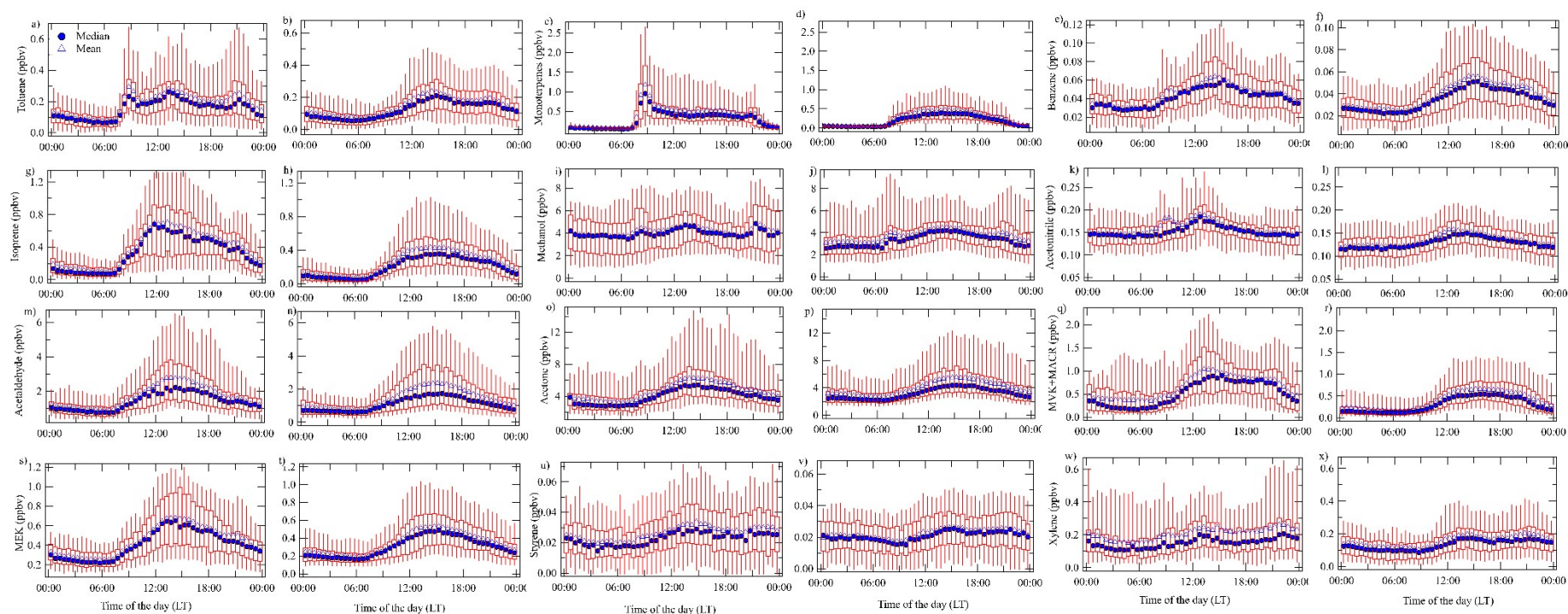


Figure S.4.1.: Box plots of the diel variation of all monitored VOCs for the days that we observe an early morning toluene peak (left) and the days when we don't observe the early morning peak in toluene (right). Units are in ppbv. (a,b) Toluene, (c,d) Monoterpenes, (e,f) Benzene, (g,h) Isoprene, (i,j) Methanol, (k,l) Acetonitrile, (m,n) Acetone, (o,p) Acetaldehyde, (q,r) MACR+MVK, (s,t) MEK, (u,v) Styrene, (w,x) Xylene. Please note that Styrene and Xylenes are below LOD. Triangles indicate the mean values, circles represent the medians, boxes show the interquartile range (IQR), and whiskers extend to the 25th and 75th percentiles.

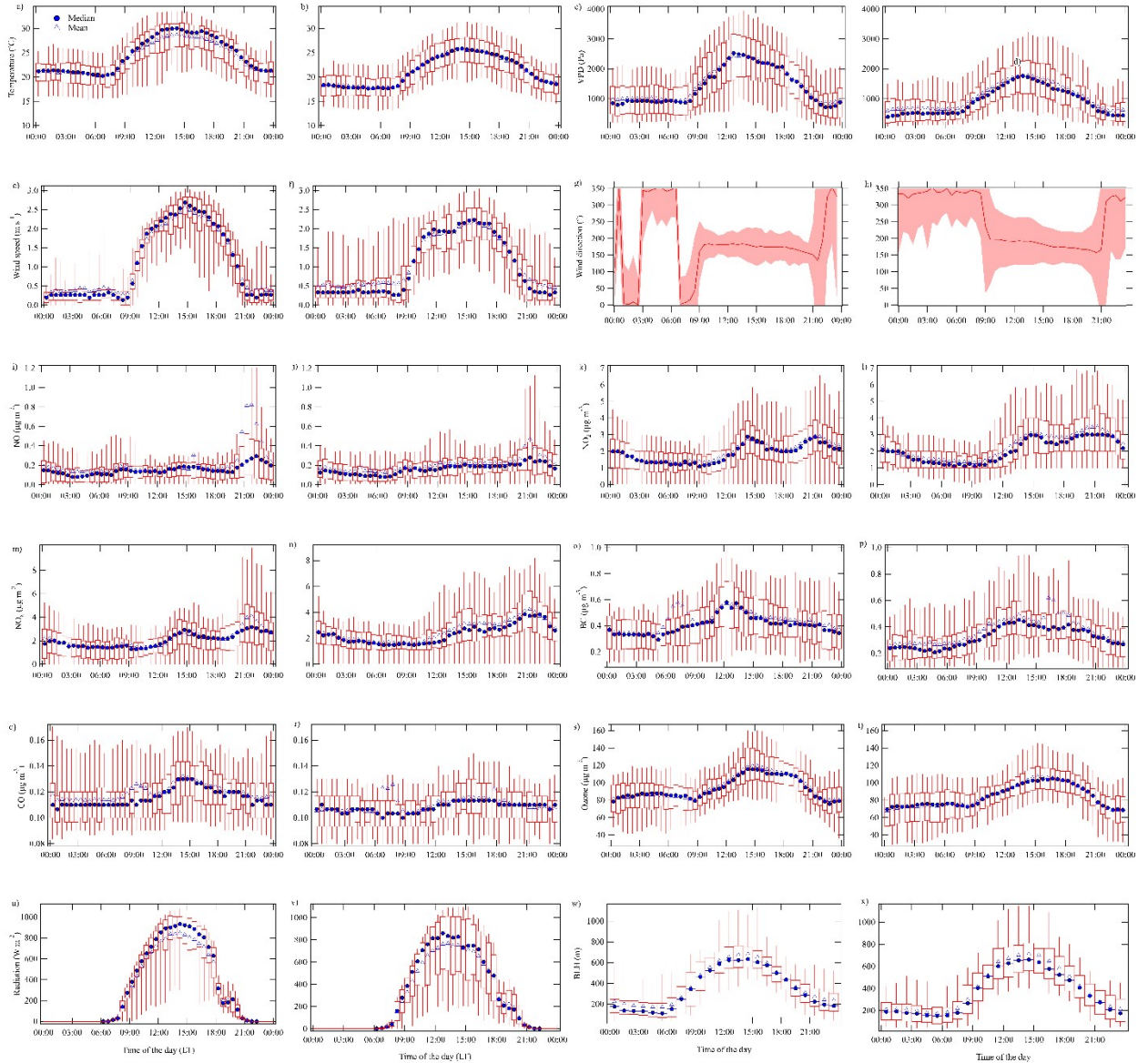


Figure S4.2.: Diurnal variation of (a,b) air temperature (in °C), VPD in Pa (c,d), wind speed in $m s^{-1}$ (e,f), wind direction in ° (g,h), NO in $\mu g m^{-3}$ (i,j), NO₂ in $\mu g m^{-3}$ (k,l), NO_x in $\mu g m^{-3}$ (m,n), black carbon (BC) in $\mu g m^{-3}$ (o,p), CO in $\mu g m^{-3}$ (q,r), ozone in $\mu g m^{-3}$ (s,t), radiation in $W m^{-2}$ (u,v) and BLH in m (w,x), measured at Montseny during days with and without toluene morning peaks (note that BLH is from Barcelona city). Triangles indicate the mean values, circles represent the medians, boxes show the interquartile range (IQR), and whiskers extend to the 25th and 75th percentiles. Note that for wind direction only averages and standard deviation is expressed.

5. Individual daily peaks

The diurnal evolution of benzene, acetonitrile, and toluene mixing ratios (ppbv) measured at the Montseny background site during the summers of 2021, 2022, and 2023 provides evidence for a

biogenic origin of the observed early-morning toluene peaks. Each individual line in the time series of Fig. S.4 represents a diurnal profile. Toluene consistently exhibits a pronounced peak between 07:00 and 10:00 LT across all three years during the summer months (June, July and August). This feature suggests a regular, non-random emission source, most likely associated with physiological responses of vegetation to increasing morning temperature, radiation, and vapor pressure deficit (VPD).

In contrast, acetonitrile, commonly used as a tracer for biomass burning (1), shows a peak only on a single day, with much lower values on all remaining days of the dataset. This isolated event likely reflects a short-lived combustion episode and does not represent a persistent source influencing the site. Benzene, a well-established anthropogenic marker typically linked to traffic emissions (2), remains relatively low and stable throughout the days. The absence of co-variation between toluene and either acetonitrile or benzene suggests that the early morning toluene peak is not associated with anthropogenic activity or long-range transport from urban areas, such as the city of Barcelona.

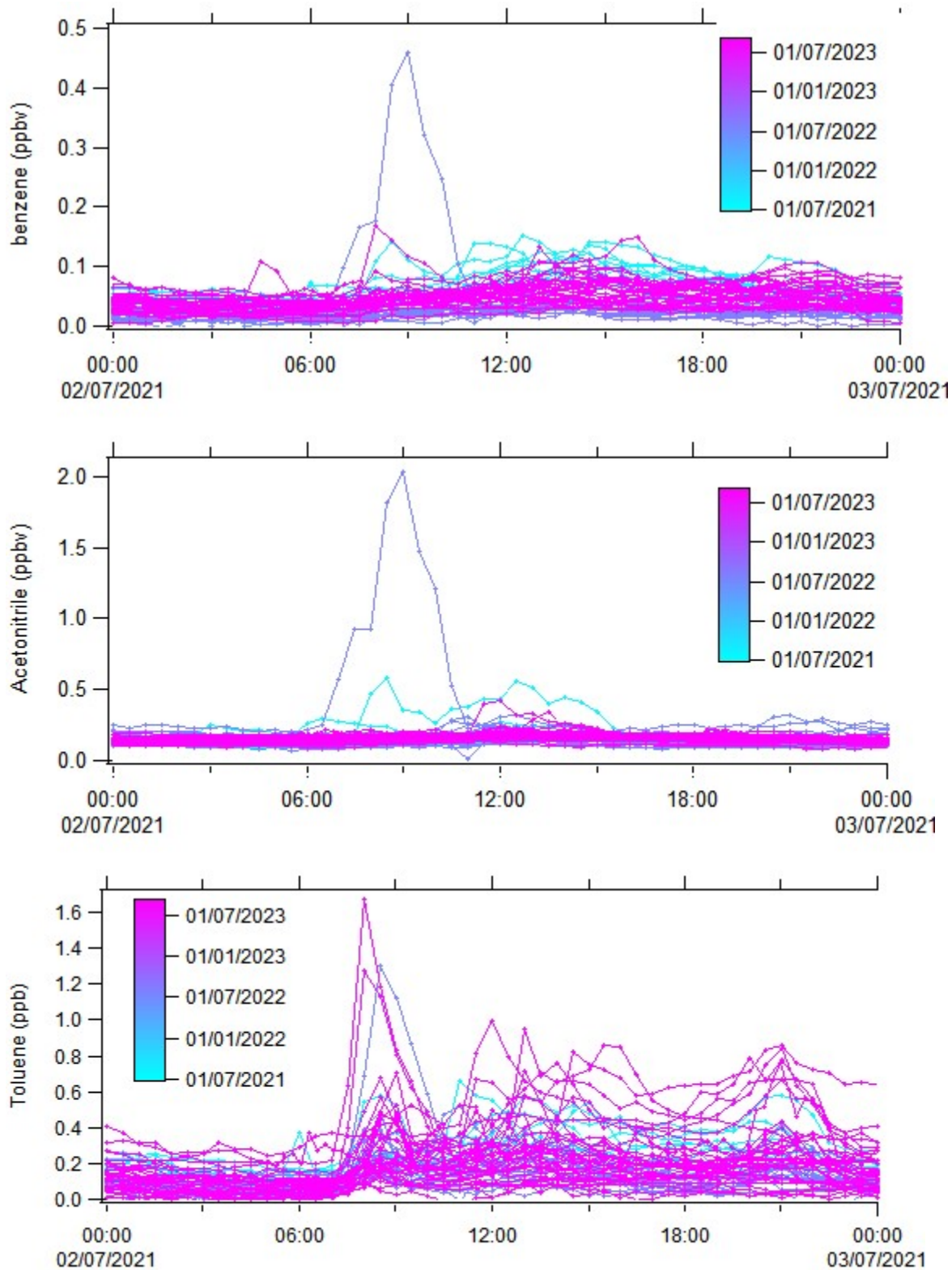


Figure S.5: All individual diel cycles for early morning toluene peak days for benzene, acetonitrile and toluene color coded by date The outlier days with early morning peak for benzene and acetonitrile are on the 26th July 2021 and the 18th July 2022.

6. Ozone dynamics: 8hr moving averages and MDA8

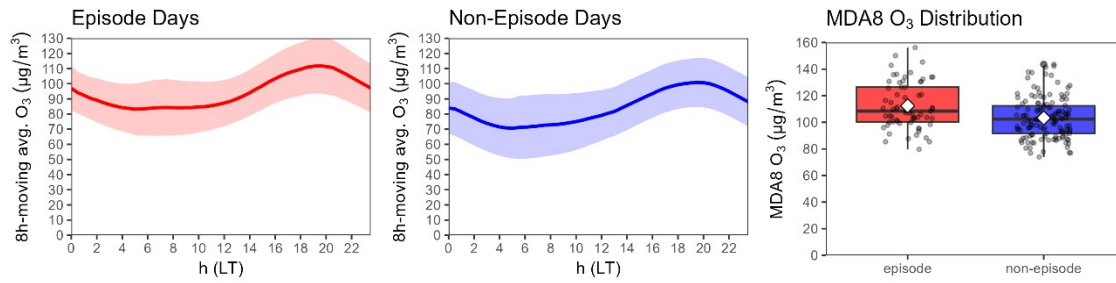


Fig. S6. Left and middle panels: diel variations of 8-h moving averages of O₃ for episode and non-episode days, respectively. Shaded ribbons indicate ± 1 standard deviation. Right panel: boxplot of the daily maximum 8-h moving averages (MDA8) of O₃, calculated according to air quality Directive 2024/2881.

Some basic statistics of the MDA8 values during episode and non-episode days.

episode	mean	median	sd	min	max	n. days
episode	112.4	108.4	17.4	79.7	156.2	65
non-episode	103.3	102.5	15.3	73.9	143.6	134

7. References

1. Wang Q, Shao M, Liu Y, William K, Paul G, Li X, et al. Impact of biomass burning on urban air quality estimated by organic tracers : Guangzhou and Beijing as cases. 2007;41:8380–90.
2. Skov H, Hansen AB, Lorenzen G, Andersen HV, Per L, Christensen CS. Benzene exposure and the effect of traffic pollution in Copenhagen , Denmark. 2001;35.