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Origin and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus)

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Section S1 Data processing and analysis of the VOCs dataset used as EPA PMF inputs

S1.1 Data preparation

The PMF analysis does not support zero and negative values or missing data. Instead, data gaps and concentrations below detection limits have been substituted following an approach developed by Hopke, 2000:

$$x_{ij} = \begin{cases} x_{ij}, \ if \ x_{ij} \geq DL_i \\ \frac{DL_i}{2}, \ if \ x_{ij} < DL_i \\ \overline{x}_i, \ if \ missing \ x_{ij} \\ \sum_{i=1}^{n} x_{ij}, \ for \ x_{TVOC,j} \end{cases}, \tag{1}$$

with DL_i and $\overline{x}_i$, respectively the analytical detection limit and the geometric mean concentration of the ith corresponding species. $TVOC$ was defined as total variable and referred to the sum of the n species including in the initial dataset. The proportion of replaced values was estimated to be less than 1 % (especially for compounds with high background mixing ratios) up to 20 %, except for pinenes and 2-methylpentane (26 % and 48 %, respectively) due to their concentrations often below the detection limit. Additionally, to avoid a too high influence of replaced points, they were downweighted, increasing associated uncertainty values (Polissar et al., 1998; Reff et al., 2007) as:

$$s_{ij} = \begin{cases} 2 \times u\left(x_{ij}\right) + \frac{DL_i}{3}, \ if \ x_{ij} \geq DL_i \\ 5 \times \frac{DL_i}{6}, \ if \ x_{ij} < DL_i \\ 4 \times \overline{x}_i, \ if \ missing \ x_{ij} \\ \sqrt{\sum_{i=1}^{n} {s_{ij}}^2}, \ for \ s_{TVOC,j} \end{cases}, \tag{2}$$

with $u\left(x_{ij}\right)$, the absolute analytical uncertainty on the ith species concentrations in the jth sample. The method to estimate the uncertainties $u\left(x_{ij}\right)$ of each sample for each species has been described in Sect. 2.2.1.

S1.2 Quality of the VOCs dataset

Besides the amount of replaced values, a compound is characterized by its signal-to-noise (S/N) ratio, which is used as an indicator of the quality of the observations (Paatero and Hopke, 2003). In EPA PMF 5.0, S/N ratios are determined from Eq. 3 (Norris et al., 2014):

$$\left(\frac{S}{N}\right)_i = \frac{1}{m}\sum_{j=1}^{m} d_{ij} \quad with \ d_{ij} = \begin{cases} \left(\frac{x_{ij}-s_{ij}}{s_{ij}}\right), & if \ x_{ij} > s_{ij} \\ 0, & if \ x_{ij} < s_{ij} \end{cases}, \tag{3}$$

where d_{ij} is the relative difference between species concentration and the corresponding uncertainty in the sample considered. Indeed, only concentration values that exceed their associated uncertainty contribute to the signal portion of the S/N calculation. According to Norris et al., 2014, S/N ratio of 1 corresponds to species with observations twice higher than uncertainties on average and consequently indicates a species with good signal quality. In this study, the data quality is qualified as:

$$\begin{cases} \left(\frac{S}{N}\right)_i \geq 1.2, \ strong\ variable\ (stayed\ unchanged) \\ 1 < \left(\frac{S}{N}\right)_i < 1.2, \ weak\ variable\ (downweighted) \\ \left(\frac{S}{N}\right)_i \leq 1, \ bad\ variable\ (excluded) \end{cases} , \quad (4)$$

Indeed, to minimize the weight of contributions of low quality species, PMF allows declaring these species as "weak" (Paatero and Hopke, 2003) and hence tripling their original uncertainties. Two species have been downweighted here (2-methylpentane and m107) due to analytical issues. No optional extra modeling uncertainty was applied here.

References:

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Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C. and Sisler, J. F.: Atmospheric aerosol over Alaska: 2. Elemental composition and sources, J. Geophys. Res. Atmospheres, 103(D15), 19045–19057, doi:10.1029/98JD01212, 1998.

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Table S1 Statistics (µg.m^{-3}), detection limits (DL - µg.m^{-}3) and relative uncertainties u(X)/X (Unc. - %) of selected VOC concentrations measured at the site.

	Species	Min	25 %	50 %	Mean	75 %	Max	σ	DL	Unc.
ALKANES	**Ethane**	1.41	2.62	2.92	3.05	3.38	6.80	0.66	0.13	6
	Propane	0.10	1.89	2.04	2.20	2.39	6.24	0.62	0.19	14
	i-Butane	0.03	0.16	0.27	0.32	0.41	1.83	0.23	0.06	8
	n-Butane	0.02	0.29	0.44	0.54	0.67	6.77	0.43	0.04	19
	i-Pentane	0.02	0.06	0.15	0.25	0.32	3.98	0.31	0.03	19
	n-Pentane	0.01	0.09	0.15	0.21	0.28	2.14	0.21	0.02	24
	2-Methylpentane	0.03	0.03	0.05	0.09	0.11	2.27	0.13	0.05	9
ALKENES	**Ethylene**	0.01	0.14	0.32	0.35	0.49	2.85	0.27	0.06	12
	Propene	0.02	0.11	0.17	0.19	0.25	1.28	0.13	0.05	31
ALKYNE	**Acetylene**	0.17	0.57	0.70	0.71	0.83	2.32	0.21	0.07	15
DIENE	**Isoprene**	0.01	0.08	0.11	0.13	0.16	0.62	0.09	0.06	11
TERPENES	**α-Pinene**	0.04	0.04	0.10	0.33	0.33	10.63	0.74	0.09	10
	β-Pinene	0.03	0.03	0.10	0.34	0.32	11.14	0.80	0.07	12
AROMATICS	**Benzene**	0.03	0.29	0.37	0.37	0.44	0.94	0.12	0.06	6
	Toluene	0.03	0.07	0.15	0.19	0.24	3.35	0.22	0.06	9
	Ethylbenzene	0.02	0.02	0.02	0.04	0.02	1.76	0.09	0.04	11
	m,p-Xylenes	0.02	0.02	0.02	0.06	0.06	3.82	0.16	0.04	12
	o-Xylene	0.02	0.02	0.02	0.03	0.02	1.77	0.08	0.03	19
ALCOHOL	**Methanol**	0.87	2.23	3.29	3.84	4.73	12.82	2.13	0.24	21
CARBONYL COMPOUNDS	**Acetaldehyde**	0.19	0.52	0.74	0.83	1.03	2.81	0.44	0.08	10
	Acetone	1.02	2.08	2.57	2.72	3.03	6.46	0.96	0.04	9
	MVK+MACR	0.01	0.06	0.08	0.09	0.11	0.41	0.06	0.01	12
	MEK	0.18	0.47	0.59	0.66	0.74	2.11	0.30	0.04	9
NITRILE	**Acetonitrile**	0.06	0.13	0.17	0.20	0.21	1.97	0.16	0.01	13

Note that, 1,3-butadiene measured at CAO was most of the time below its detection limit and up to 0.09 µg.m^{-3}.

Figure S1 Instrument status indicating the period when each gas, aerosol and meteorological instrument was operating

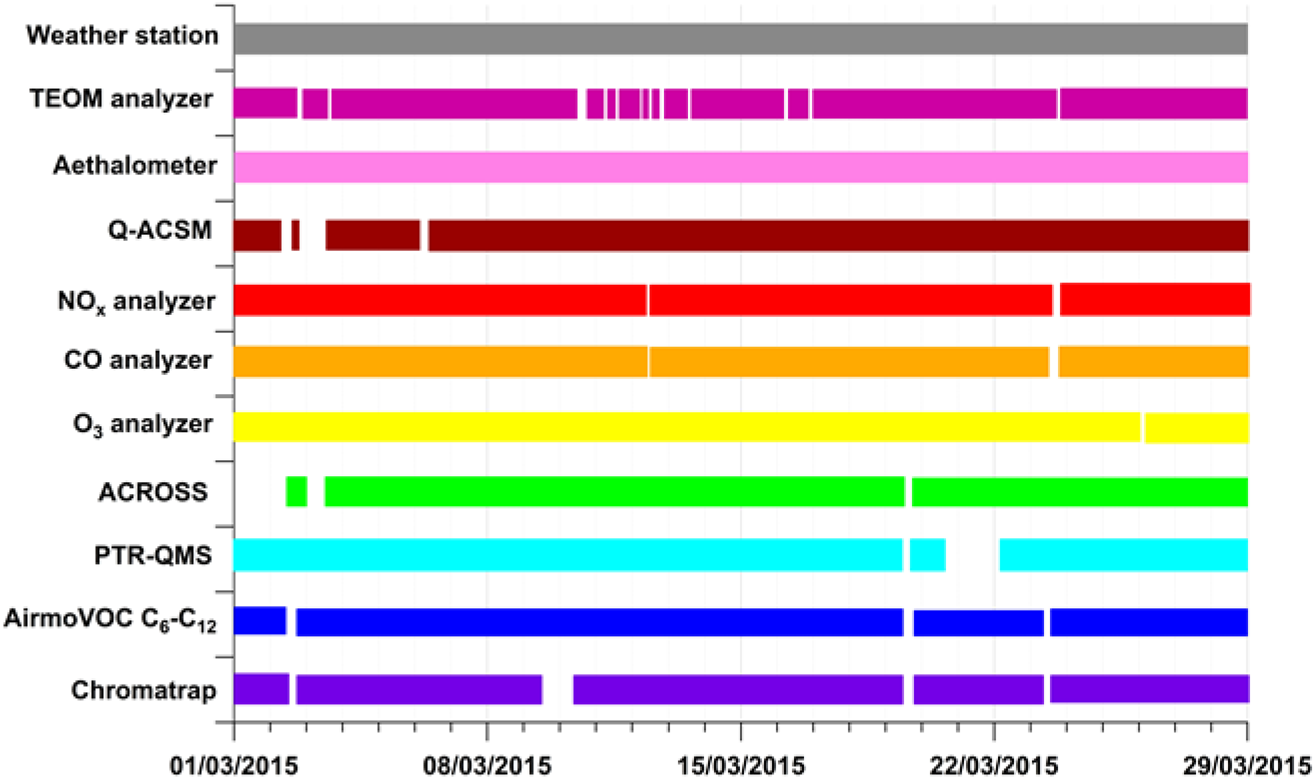


Figure S2 Wind roses in function of air mass origins and time periods.

Contribution expressed in % corresponds to the frequency of occurrence in a wind direction. Day and night wind roses don’t include data associated to C7. Time is given as local time. C0 – Local; C1 – N. Africa; C2 – marine air masses; C3 – Europe; C4 – NW. Asia; C5 – W. of Turkey; C7 – SW. Asia

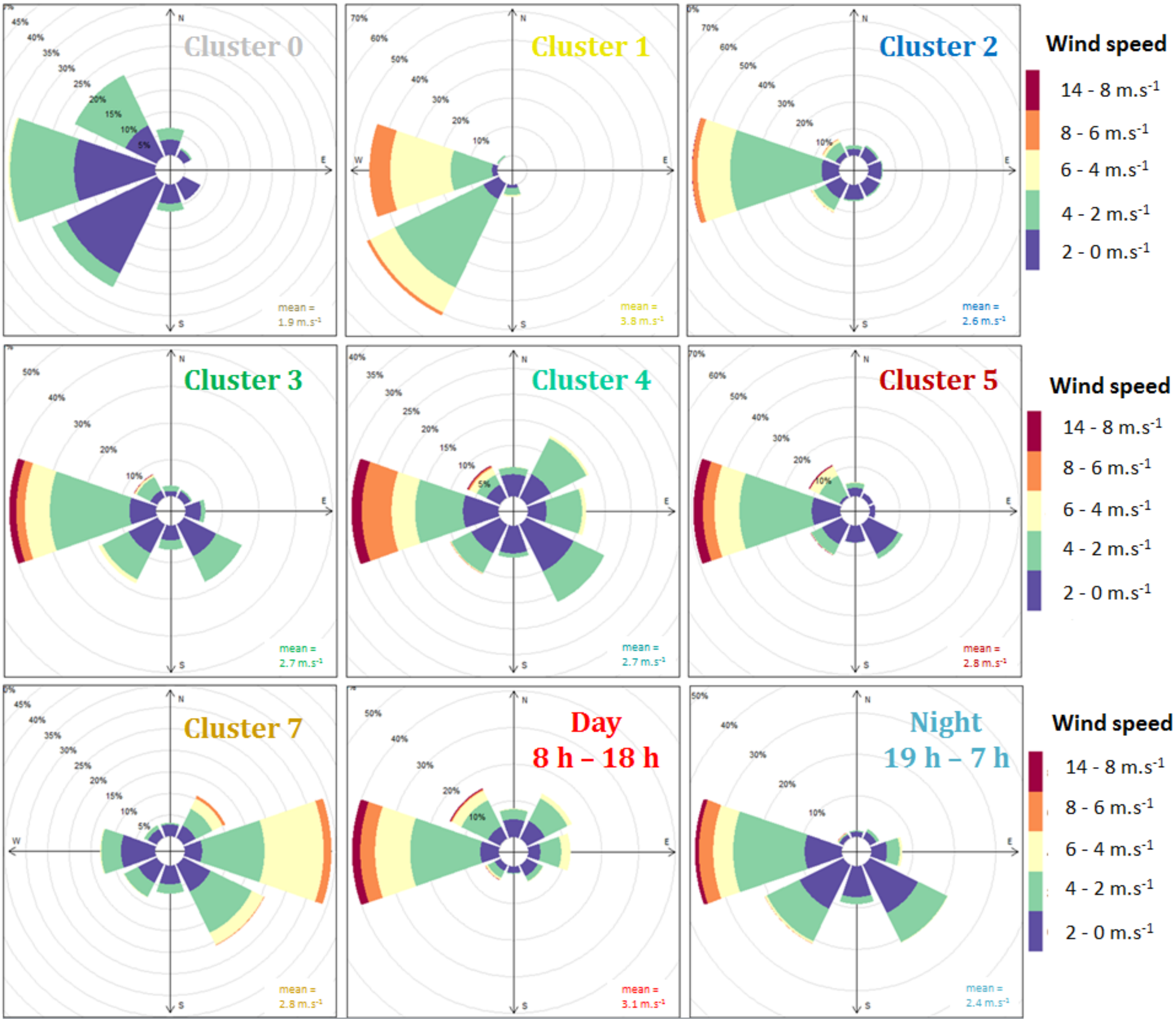


Figure S3 Time serie of gas tracers (Ozone, CO, NO and NO_2 – black and grey colors) in relation to air mass origins and temperature.

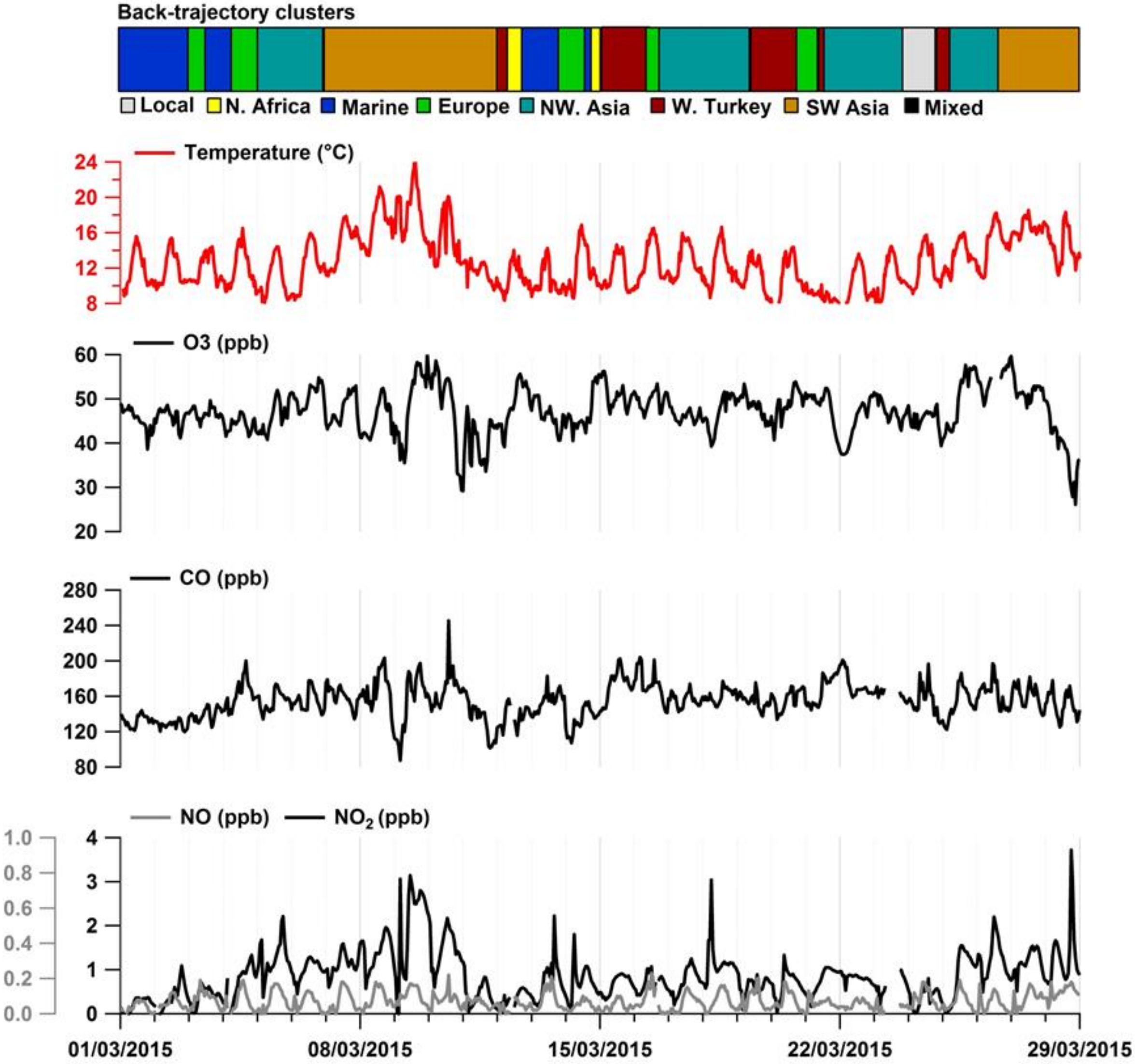


Figure S4 Time of aerosol tracers ($PM_{2.5}$, PM_{10}, BC, BC fuel and BC wood burning – blue and black colors) in relation to air mass origins and temperature.

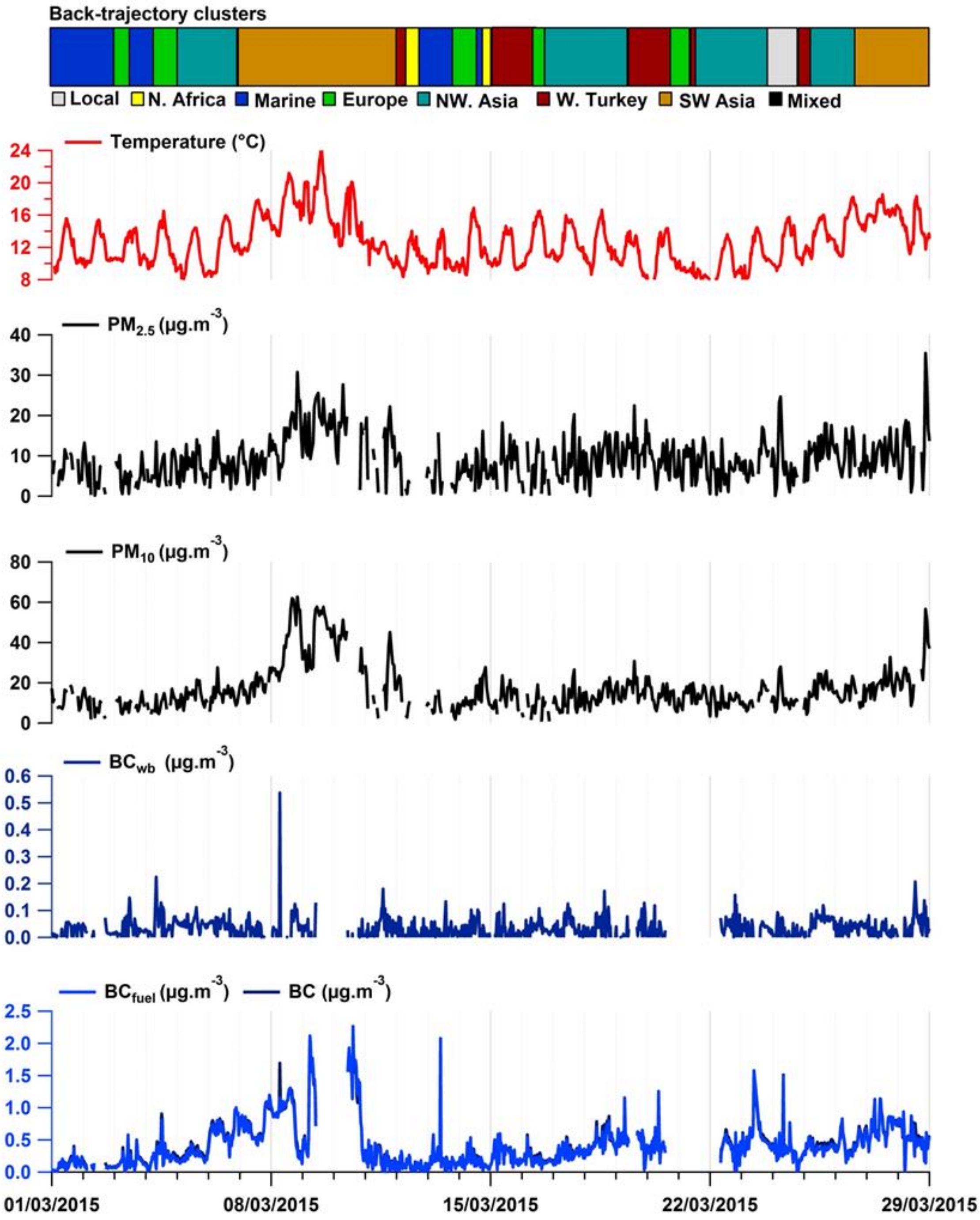


Figure S5 Rose of the CPF for VOCs factors 1 & 2 in function of vegetation

Credit picture: Vegetation map of Cyprus (Natural resource information and remote sensing center 1998).

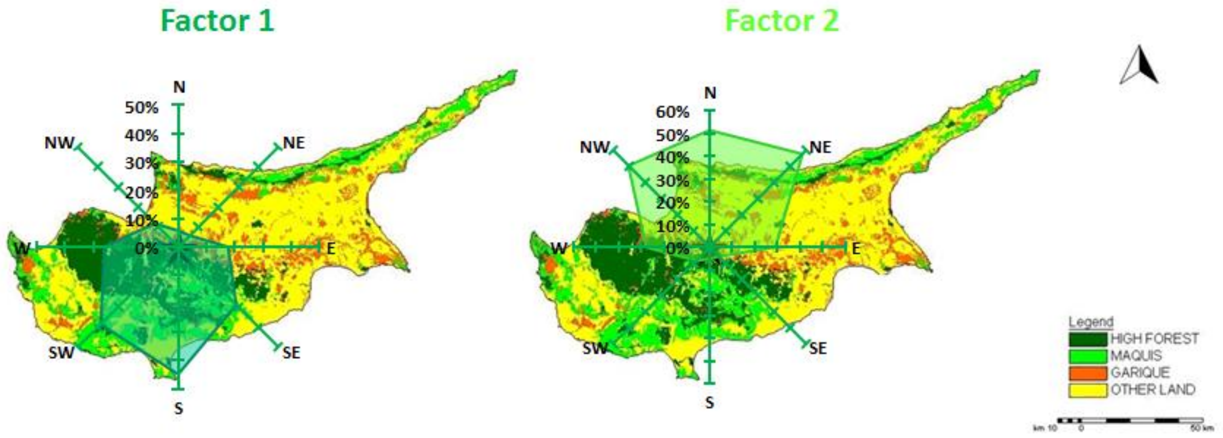


Figure S6 Potential source areas contributing to the 3 anthropogenic VOCs factors, determined using the CF model 5-days back-trajectories from HYSPLIT model, as a function of air masses origin.

Contributions are in µg.m^{-3}. Cluster 0 – Local; Cluster 1 – N. Africa; Cluster 2 – marine air masses; Cluster 3 – Europe; Cluster 4 – NW Asia; Cluster 5 – West of Turkey; Cluster 7 – SW Asia.

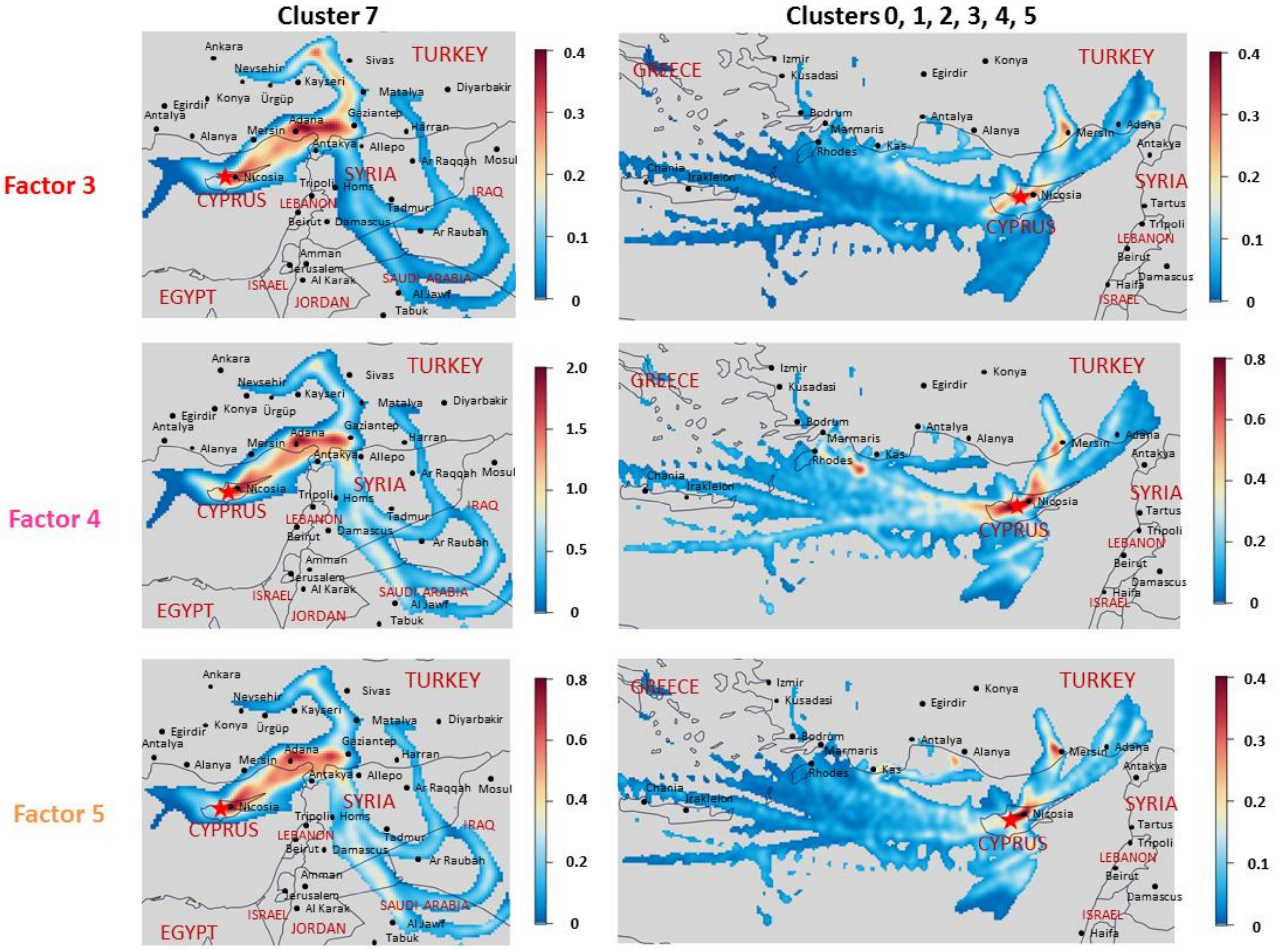


Figure S7 Time series of PMF factor relative contribution.

Factor 1 - biogenic source 1; factor 2 - biogenic source 2; factor 3 – short-lived combustion source; factor 4 – evaporative sources; factor 5 – industrial and evaporative sources; factor 6 – regional background.

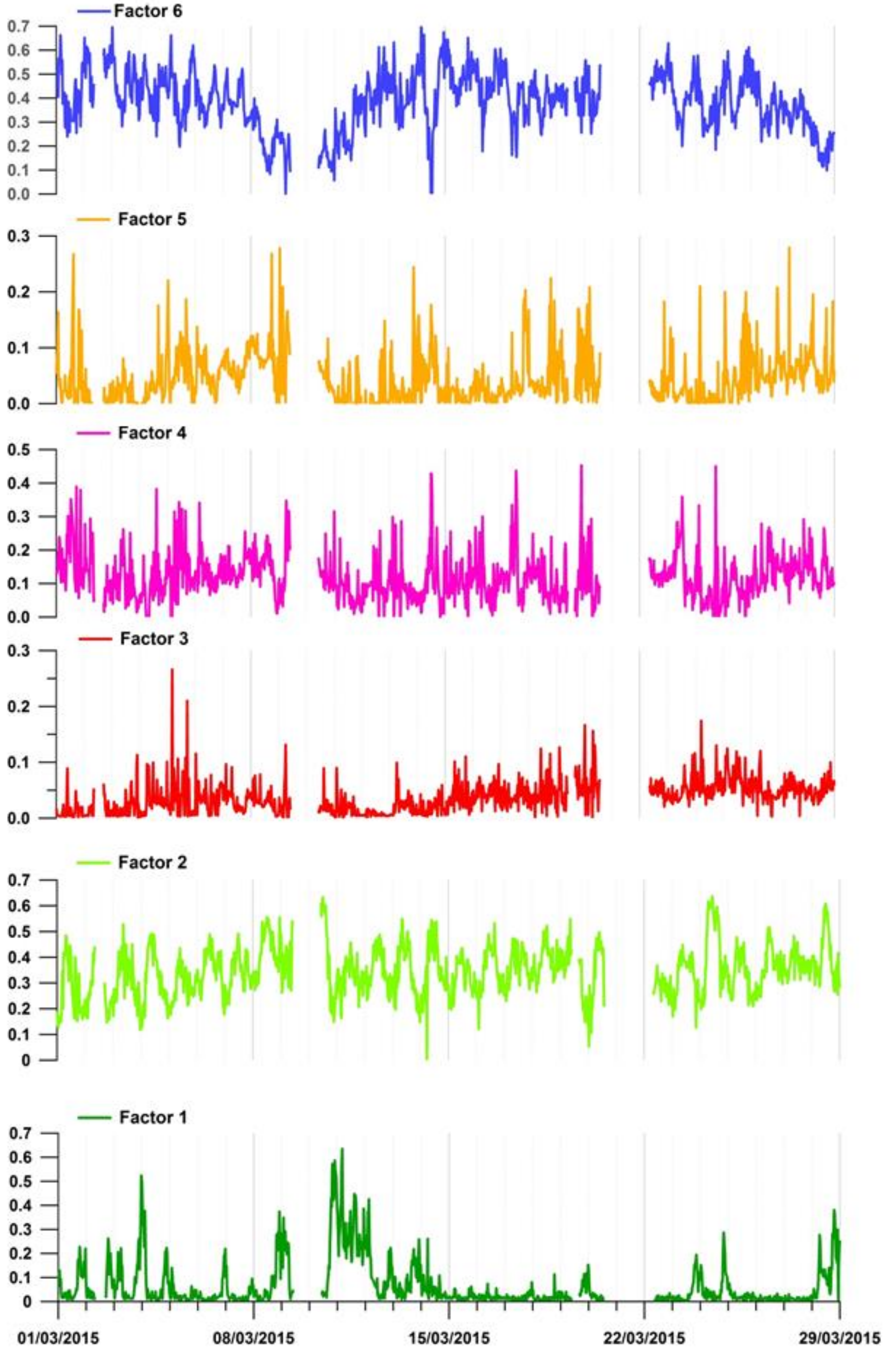
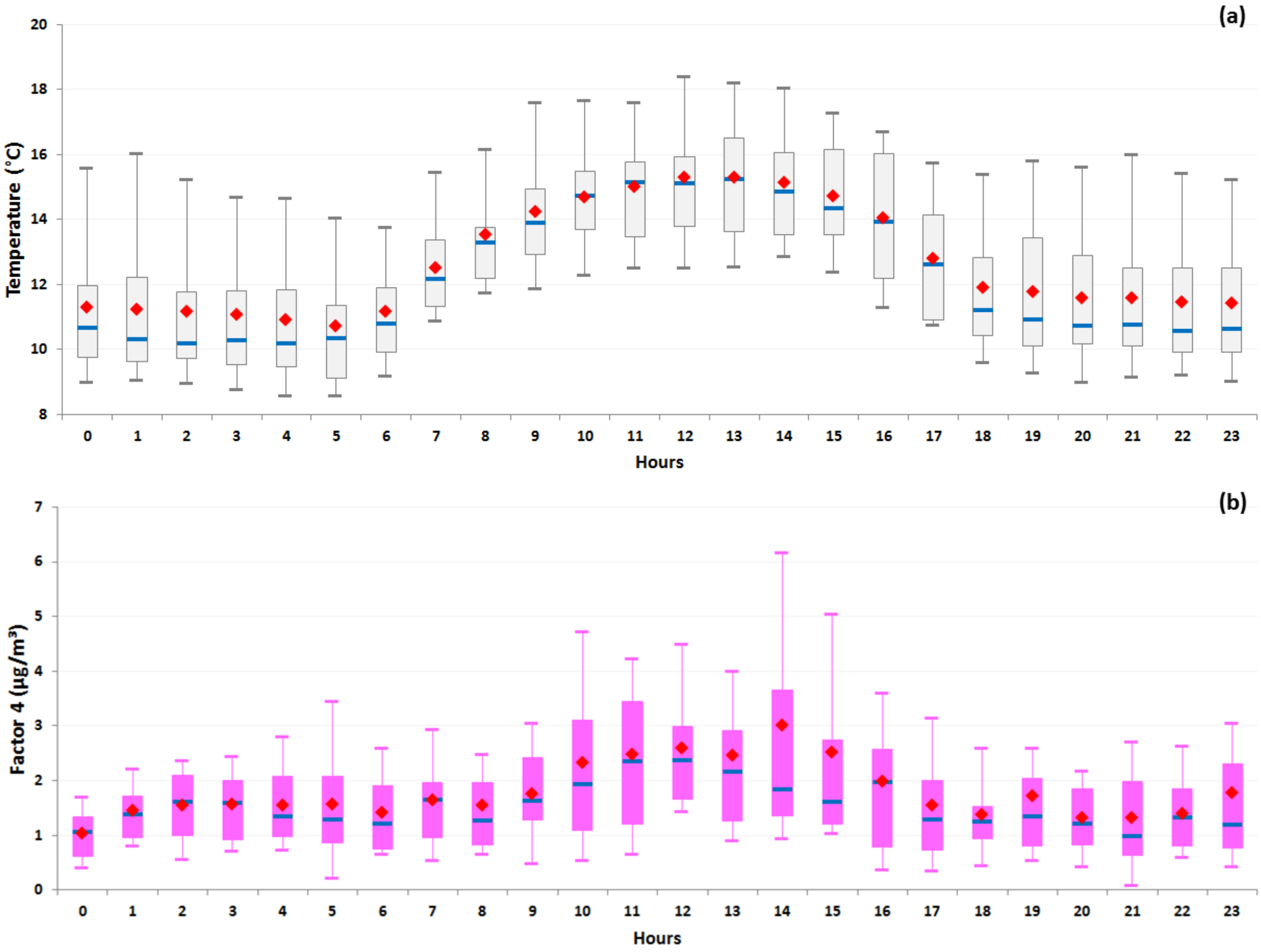
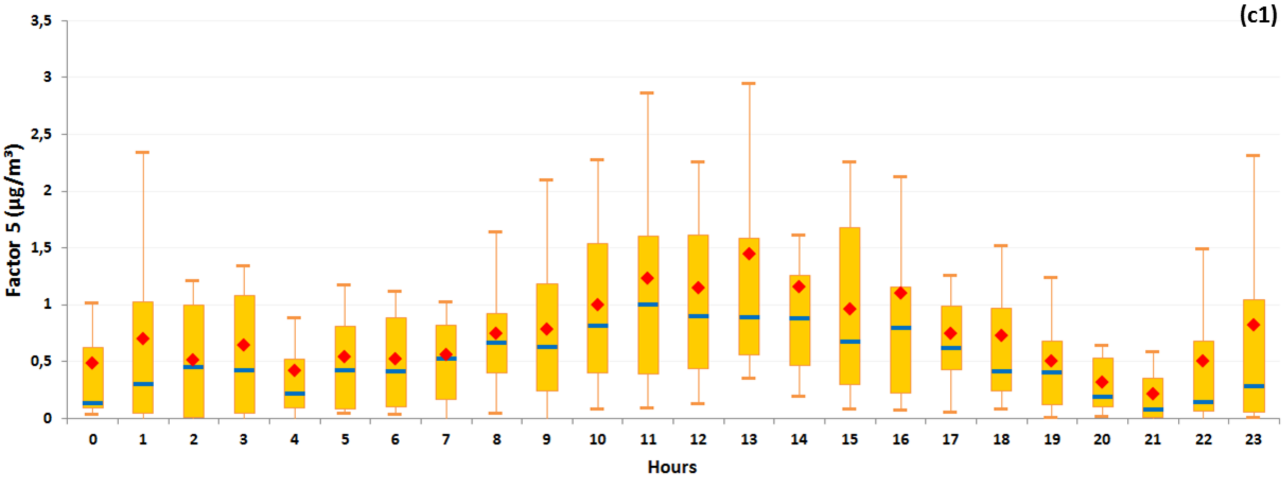


Figure S8 Diel variation of the factor contributions (b and c) and temperature (a) represented by hourly box plots.

Factor 5 results are represented in two figures in function of wind direction sectors: c1 only with South and Southeast directions and c2 with the others. Diel profiles don’t include contributions obtained when the site was under the influence of air masses categorized in “Southwest Asia” cluster (see section 3.5.2.). Blue solid line represents the median contribution, the red marker represents the mean contribution and the box shows the interquartile range. The bottom and the top of box depict the first and the third quartiles (i. e. Q1 and Q3). The ends of the whiskers correspond to first and the ninth deciles (i. e. D1 and D9). Time is given as local time.




(c1)
Factor 5 (µg/m³)
3,5
3
2,5
2
1,5
1
0,5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
Hours

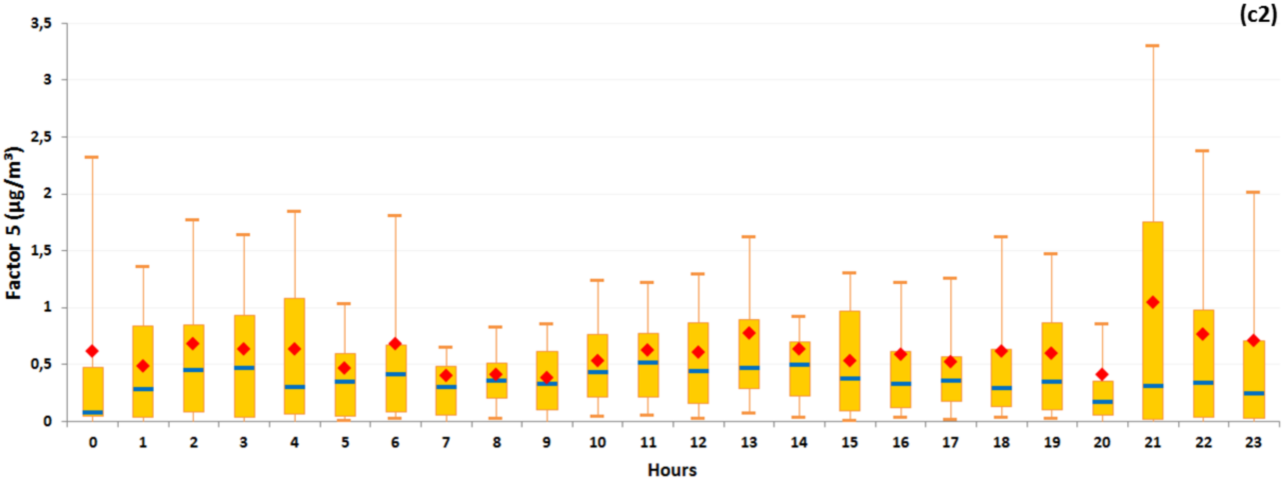

(c2)
Factor 5 (µg/m³)
3,5
3
2,5
2
1,5
1
0,5
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
Hours

Figure S9 Mass spectra profile obtained for the 3 factor constrained PMF solution.

OA factors: HOA - hydrogen-like OA; SV-OOA – semi-volatile oxygen-like OA; LV-OOA – low-volatile oxygen-like OA.

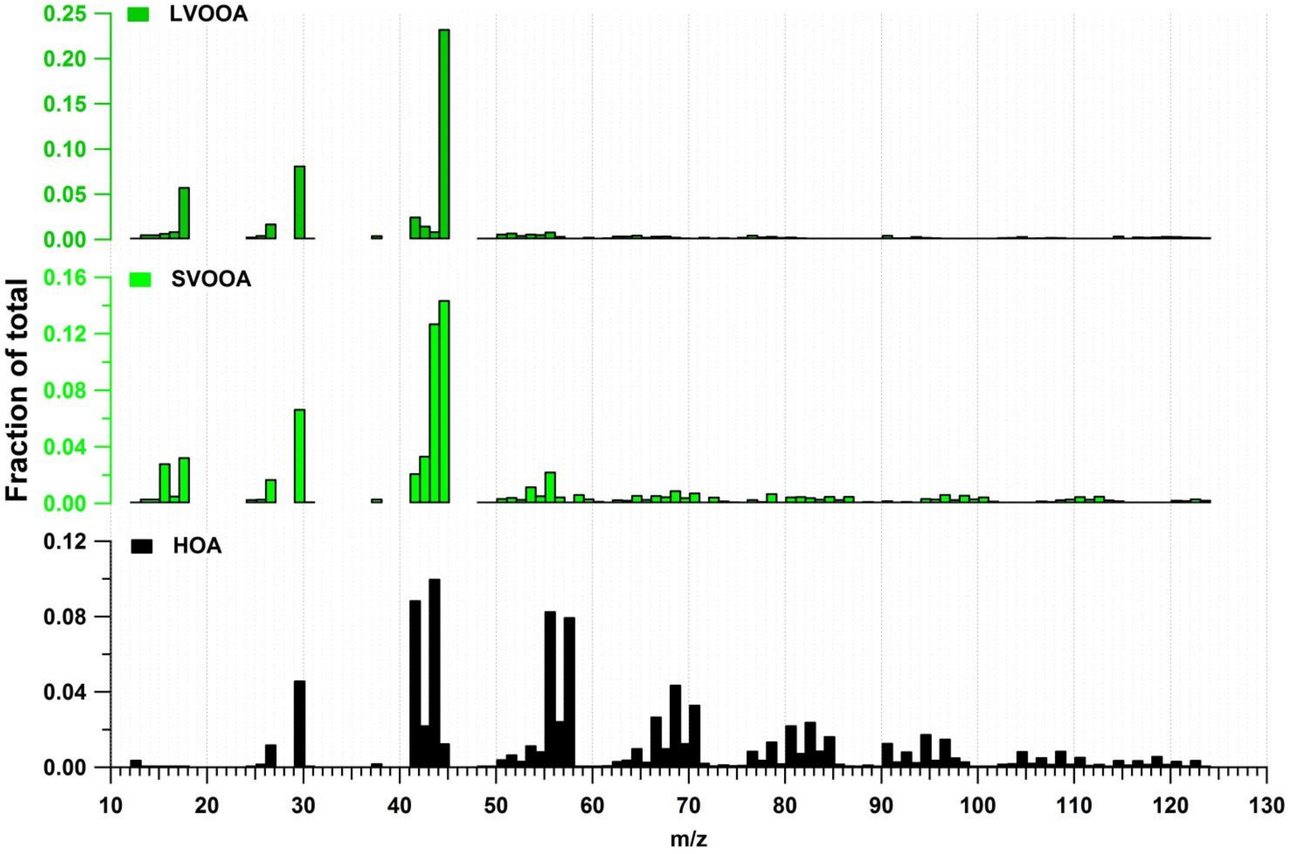
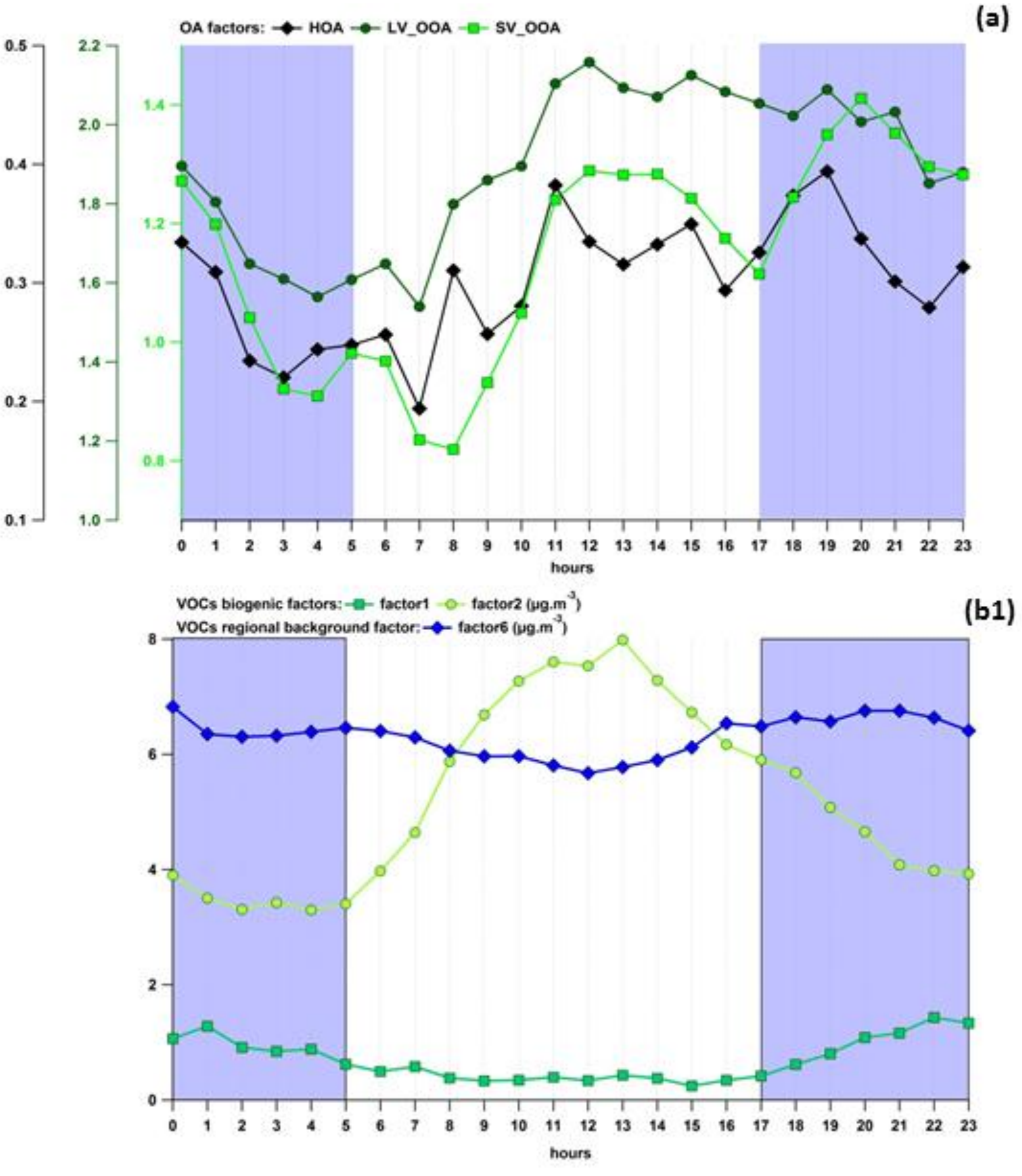
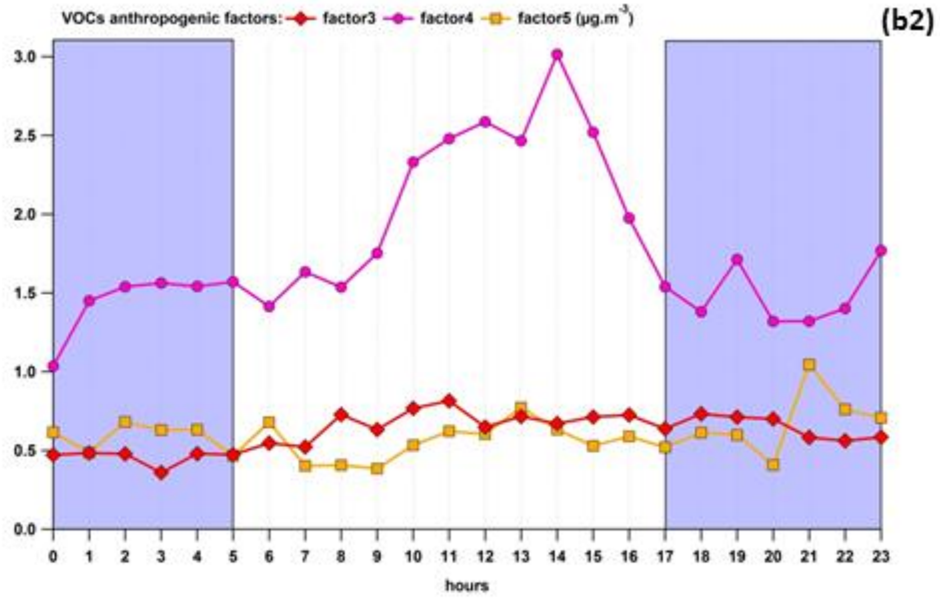


Figure S10 Diel variation of the OA and VOCs factor contributions represented by average contributions.

Time is given as local time. OA factors (a): HOA - hydrogen-like OA; SV-OOA – semi-volatile oxygen-like OA; LV-OOA – low-volatile oxygen-like OA. VOCs factors (b1 and b2): Factor 1 - biogenic source 1; factor 2 - biogenic source 2; factor 3 – short-lived combustion source; factor 4 – evaporative sources; factor 5 – industrial and evaporative sources; factor 6 – regional background.




VOCs anthropogenic factors: factor3 factor4 factor5 (µg.m^{-3})
(b2)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
hours