S1 Air mass history examples from UK NAME dispersion model
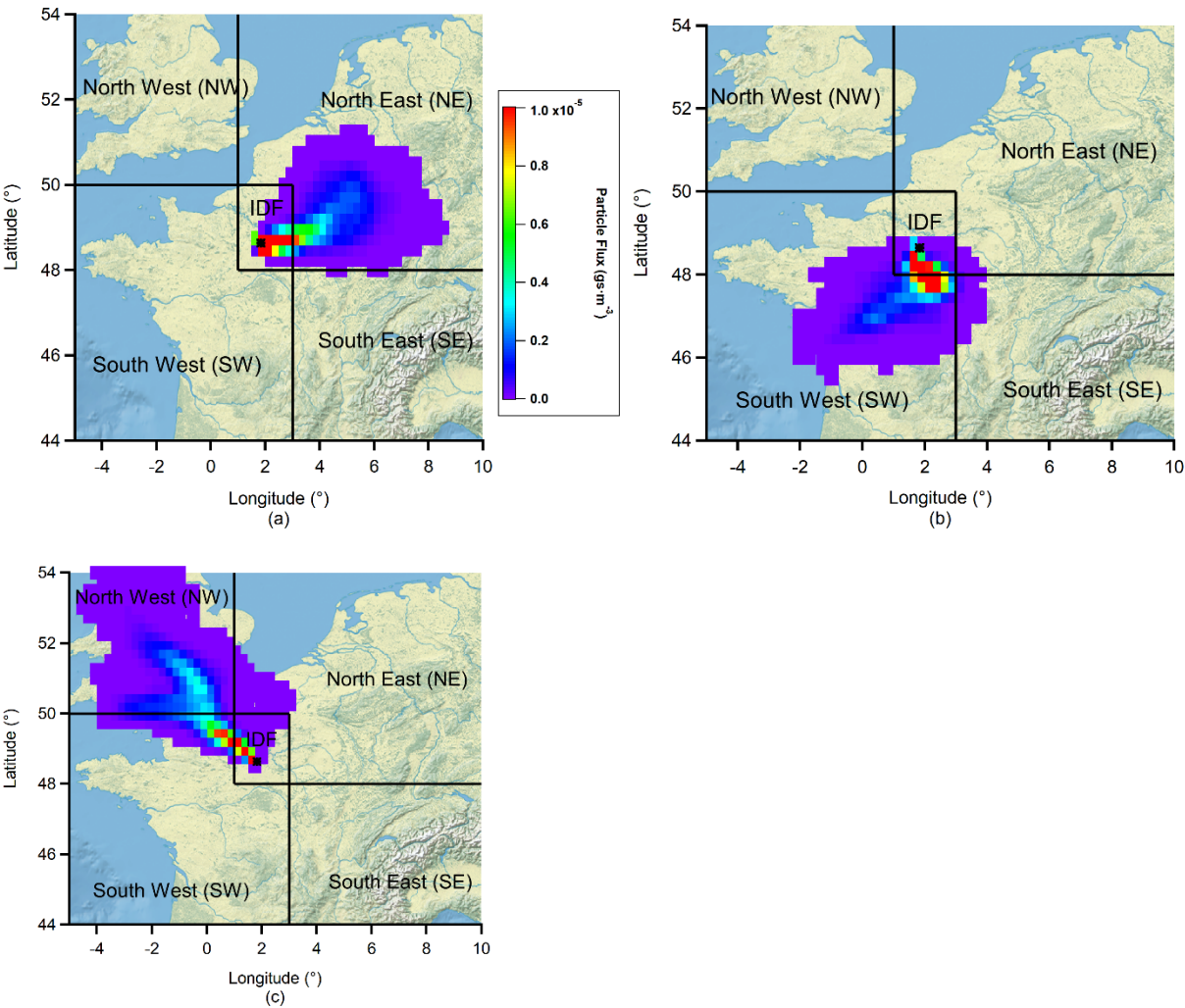
Figure S1: Examples of different external air mass sources dominated periods: (a) Northeast (NE) airmass-dominated period (12:00 UTC 11/07/2022); (b) Southwest (SW) airmass-dominated period (12:00 UTC 01/07/2022); and (c) Northwest (NW) airmass-dominated period (12:00 UTC 05/07/2022).

S2 Spatial distribution of fire points
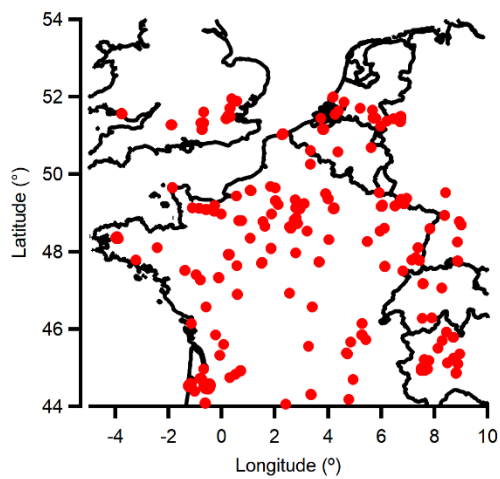
Figure S2: Spatial distribution of fire points during the ACROSS project period observed by MODIS.

S3 Positive Matrix Factory analysis from HR-AMS

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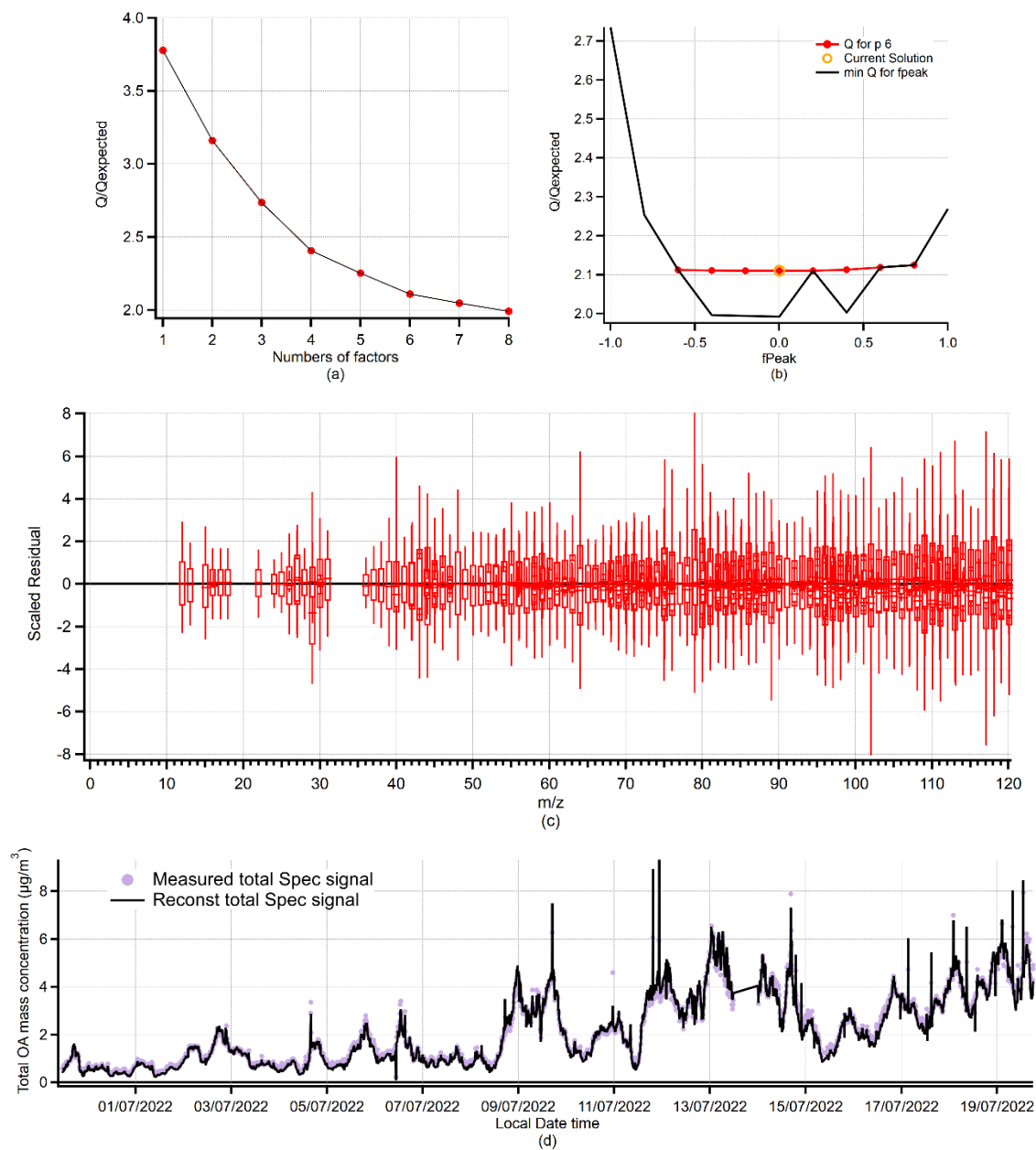
Figure S3: PMF diagnostic plots: (a) Quality-of-fit parameter Q/Q$_{expected}$ varied as a function of the number of factors, (b) Q/Q$_{expected}$ varied as a function of fpeak, (c) scaled residual for each m/z, (d) time series of measured and PMF reconstructed OA mass concentrations.
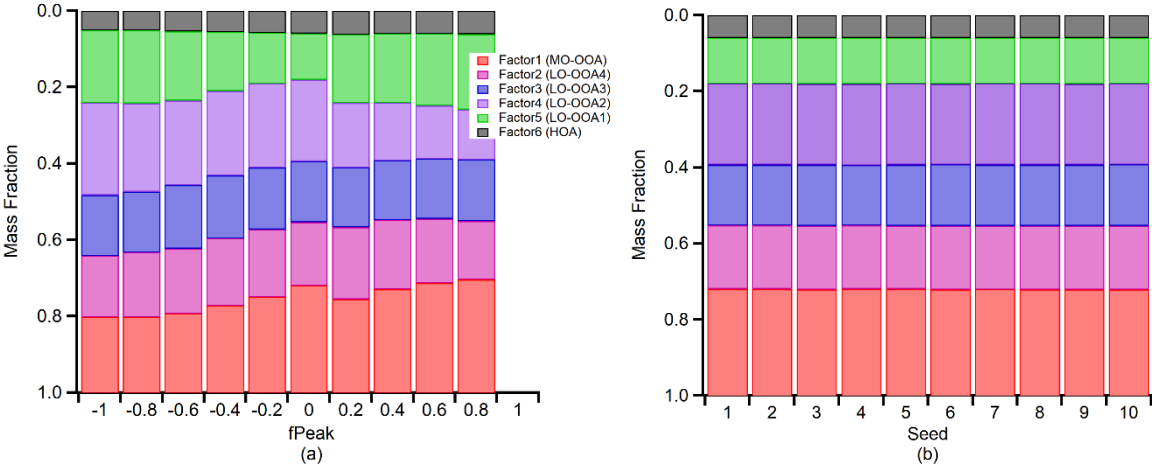
Figure S4: Mass fraction of PMF factors for six-factor solution as a function of (a) fPeak, (b) Seed.
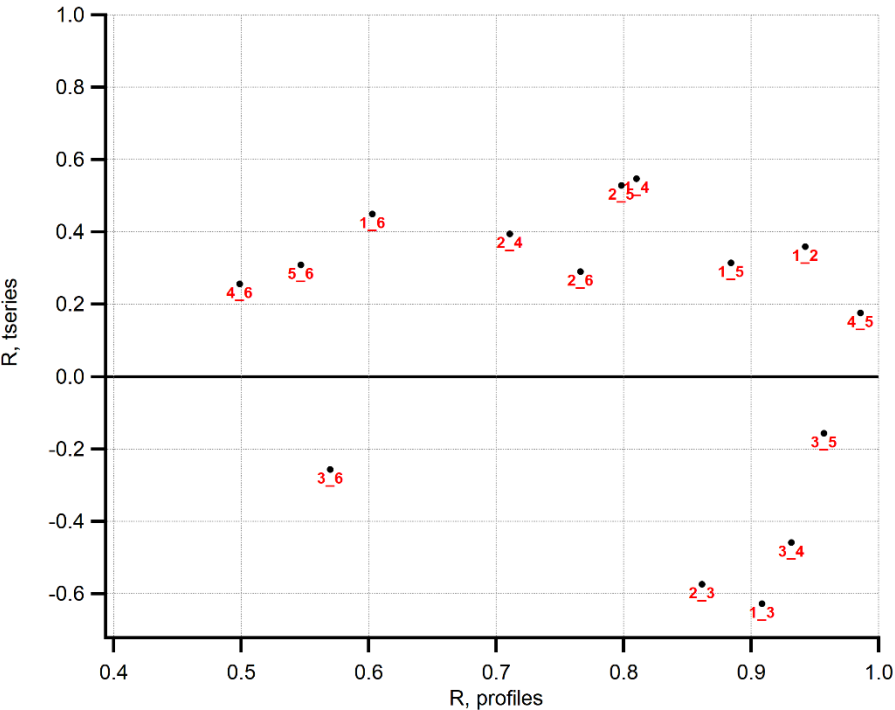
Figure S5: Correlations of the time series and spectral profiles among the PMF factors. The factor numbers refer to: (1) MO-OOA; (2) LO-OOA4; (3) LO-OOA3; (4) LO-OOA2; (5) LO-OOA1; (6) HOA

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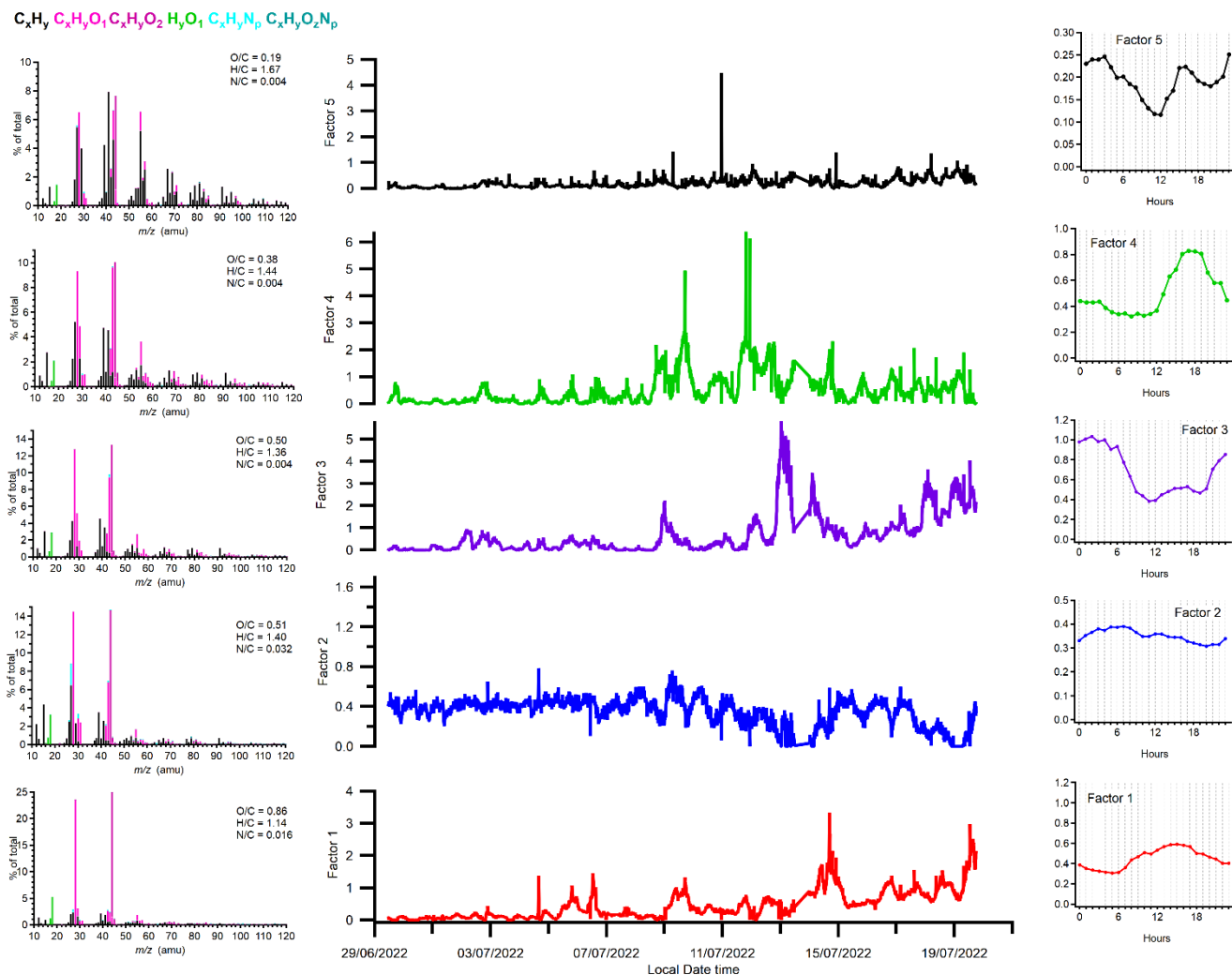
Figure S6: The average mass spectra and time series for 5-factor solution. Factor 4 is a mixed factor of LO-OOA1 and LO-OOA4. The HOA factor is not distinctly resolved in the 5-factor solution because Factor 5 represents a mixture of HOA and secondary compounds. This is evidenced by its afternoon concentration peak which is similar to the other OOA factors.

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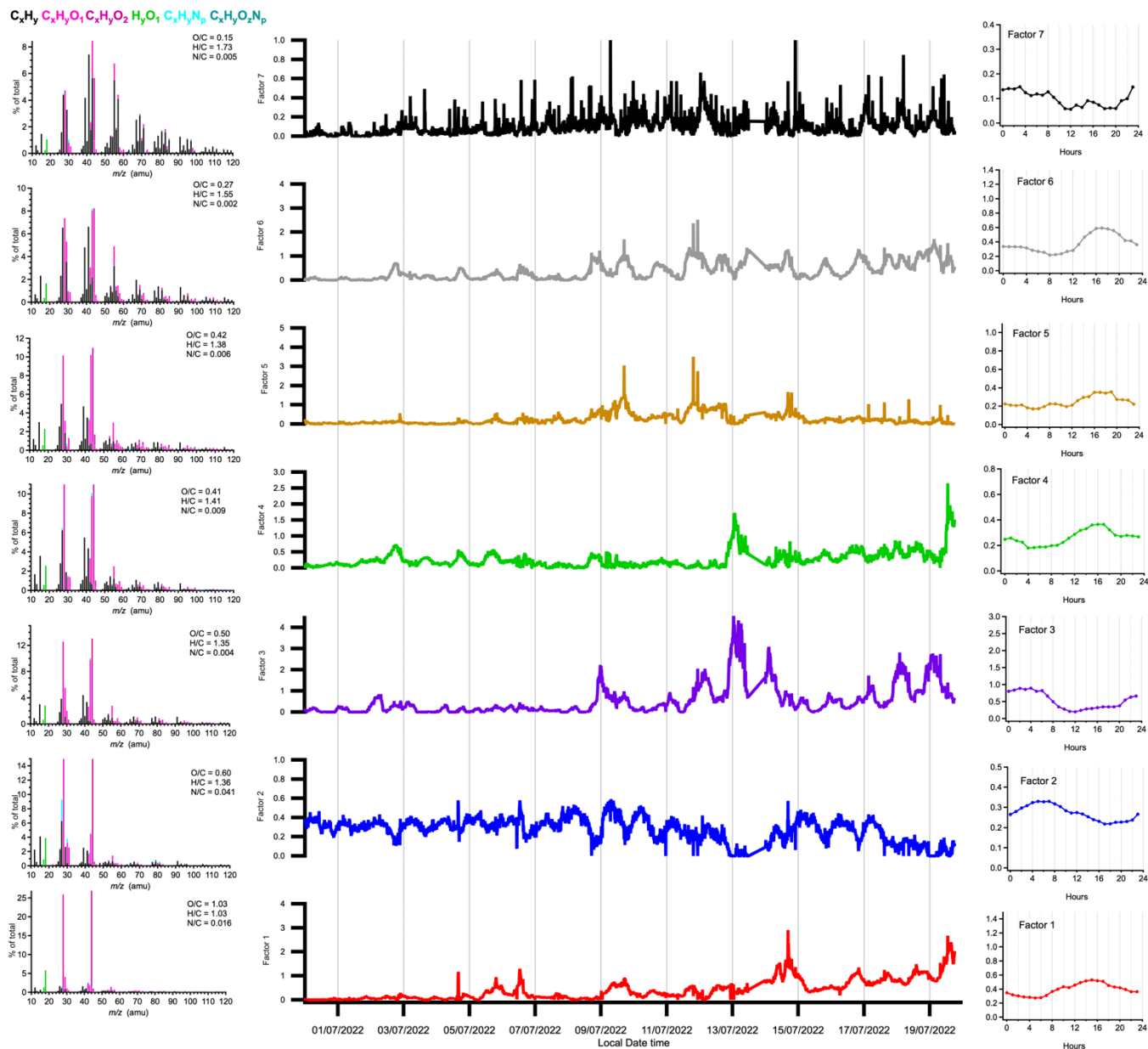
Figure S7: The average mass spectra and time series for 7-factor solution. The LO-OOA1 splits into two factors (Factor 3 and Factor 5). The 7-factor solution exhibited greater rotational ambiguity, as indicated by significant variation in factor mass fractions across the fPeak range (-1 to 1).

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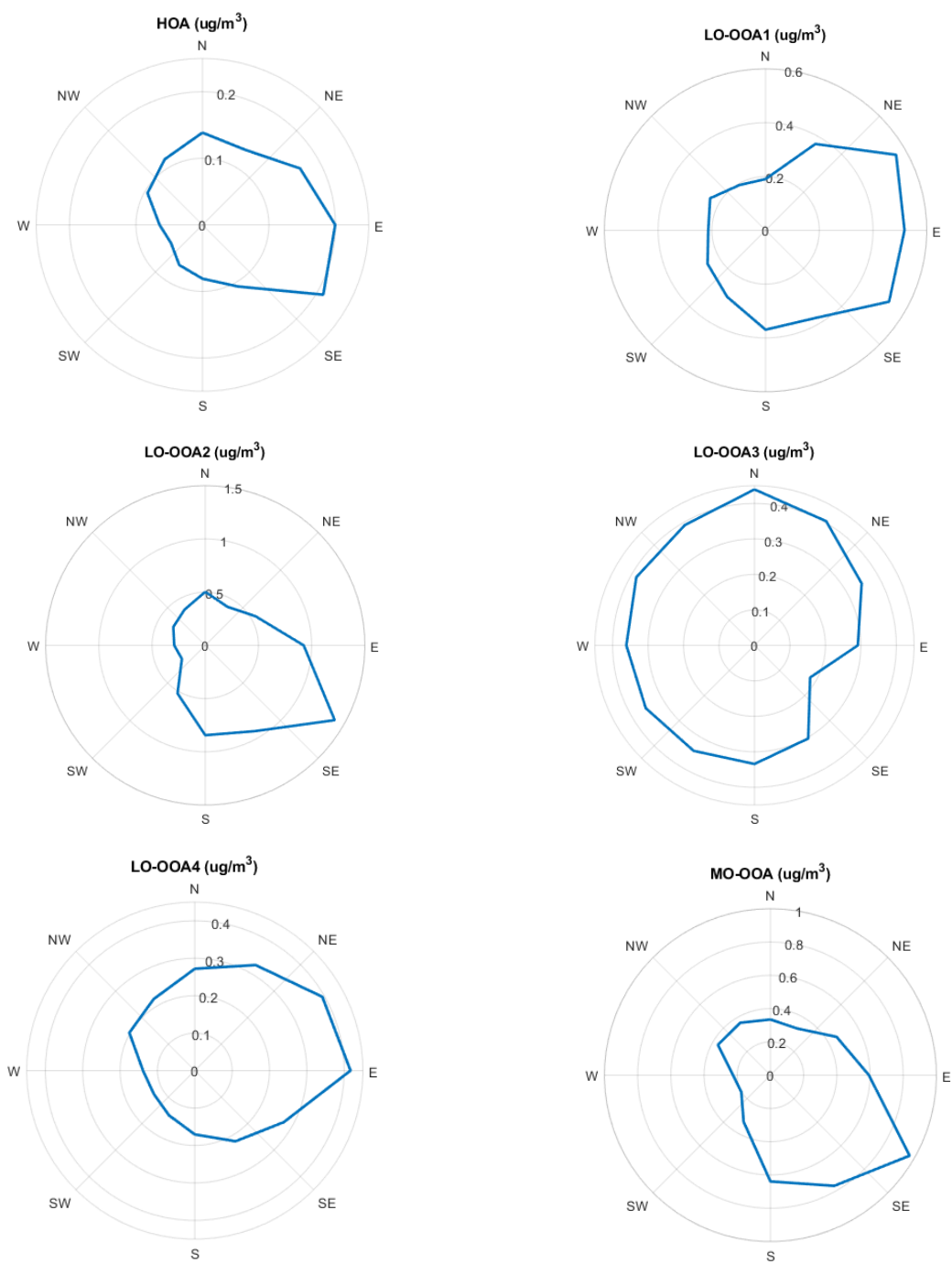


Figure S8: Wind rose for the PMF factors.

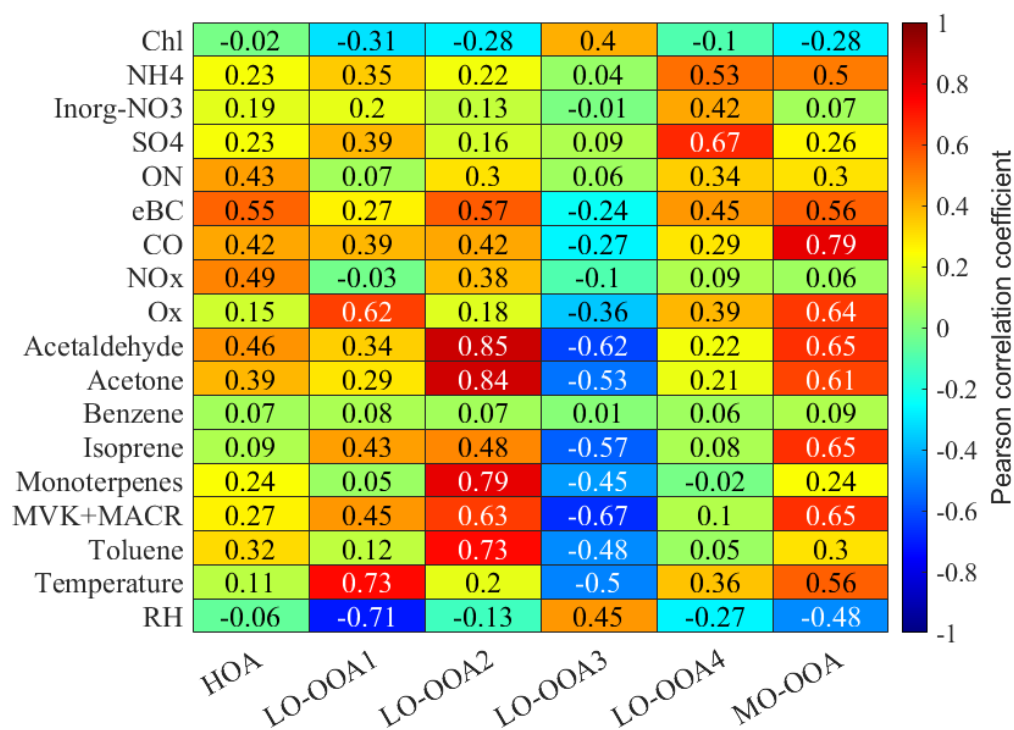
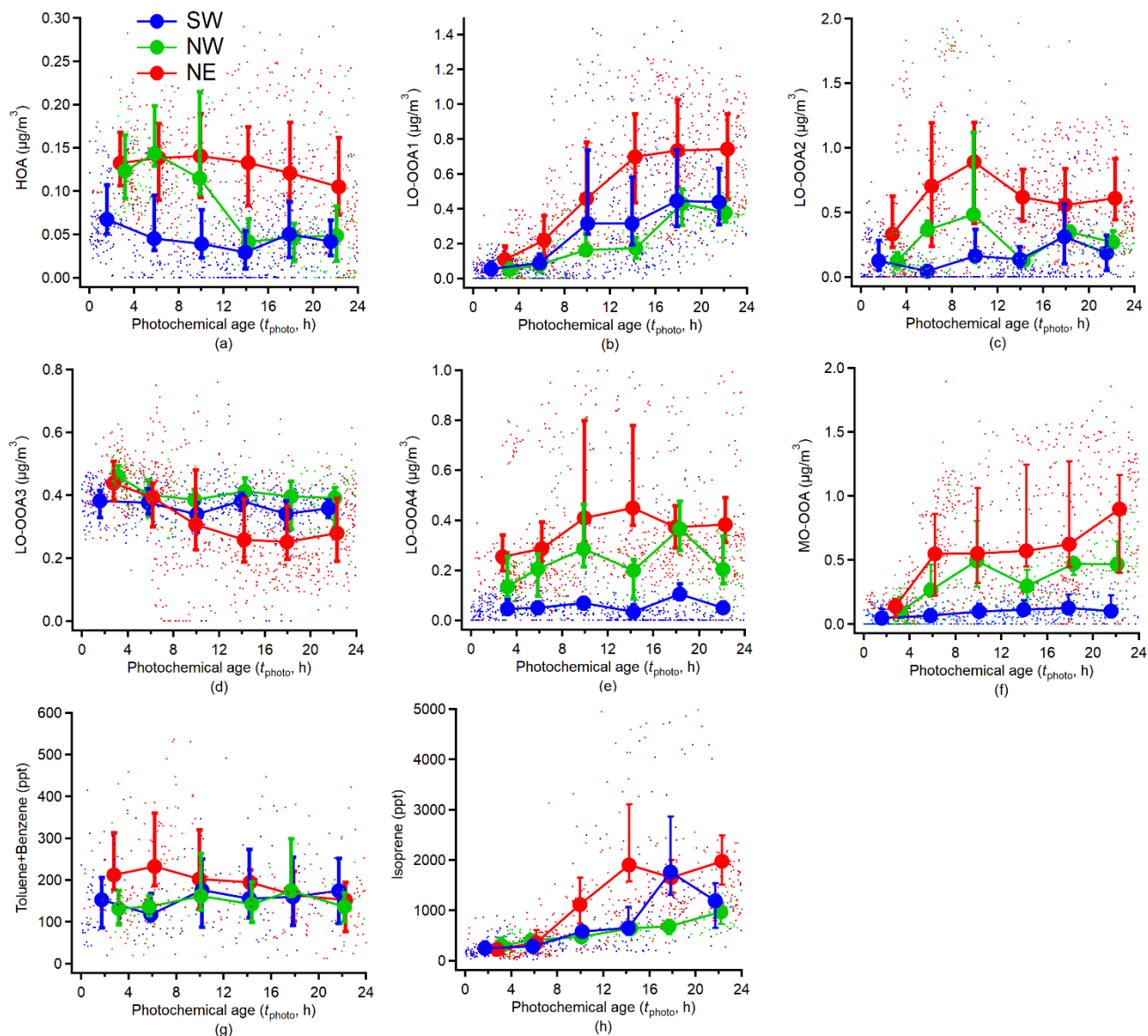



Figure S9: Person correlation coefficient (r) between the AMS PMF factors and the external tracers

50   Figure S10: Variations in (a-g) HR-AMS PMF-derived factors concentrations; (h) Sum of Toluene and Benzene concentration; (i) isoprene concentration as a function of photochemical age. The error bar indicates the 25th and 75th percentiles, respectively.

Normalised Parameters	Southwest (SW) period	Northwest (NW) period	Northeast (NE) period
PM$_1$	$y = 23 \cdot \exp\big(0.038(\pm0.005)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.97$	$y = 25.41 \cdot \exp\big(0.025(\pm0.003)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.97$	$y = 27.7 \cdot \exp\big(0.029(\pm0.007)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.91$
Total OA	$y = 12.8 \cdot \exp\big(0.050(\pm0.005)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.98$	$y = 15.12 \cdot \exp\big(0.035(\pm0.003)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.99$	$y = 18.56 \cdot \exp\big(0.037(\pm0.011)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.87$
HOA	-	$y = 1.61 \cdot \exp\big(-0.068(\pm0.017)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.91$	-
LO-OOA1	$y = 0.91 \cdot \exp\big(0.080(\pm0.02)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.93$	$y = 0.59 \cdot \exp\big(0.081(\pm0.02)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.92$	$y = 1.62 \cdot \exp\big(0.066(\pm0.03)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.76$
LO-OOA2	$y = 0.97 \cdot \exp\big(0.053(\pm0.027)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.69$	$y = 1.26 \cdot \exp\big(0.043(\pm0.02)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.72$	$y = 2.91 \cdot \exp\big(0.026(\pm0.005)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.47$
LO-OOA3	-	-	$y = 3.81 \cdot \exp\big(-0.029(\pm0.014)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.67$
LO-OOA4	-	$y = 1.50 \cdot \exp\big(0.032(\pm0.007)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.49$	$y = 1.82 \cdot \exp\big(0.029(\pm0.011)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.59$
MO-OOA	$y = 0.70 \cdot \exp\big(0.048(\pm0.021)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.76$	$y = 1.25 \cdot \exp\big(0.064(\pm0.015)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.92$	$y = 1.58 \cdot \exp\big(0.064(\pm0.013)$ $\cdot t_{\text{photo}}\big)$ $R^2 = 0.93$

Table S1 Fitting functions for the different parameters as a function of relative photochemical age.

HR-AMS PMF factor	$\sigma_{abs\ BrC,470}$ ($R^2 = 0.54$)	
	Regression coefficient a_i	Partial correlation coefficient
HOA	0.49	0.53
LO-OOA1	-0.06	0.39
LO-OOA2	0.03	0.58
LO-OOA3	0.49	-0.25
LO-OOA4	0.34	0.55
MO-OOA	0.40	0.86
Intercept	-0.08	

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Table S2 Results of multiple linear regression (MLR) between $\sigma_{abs\ BrC,470}$ and individual PMF-derived factors including. All the PMF-derived factors are included here.