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Measurements of the aerosol chemical composition and mixing state in the Po Valley using multiple spectroscopic techniques

S. Decesari et al.

Correspondence to: S. Decesari (s.decesari@isac.cnr.it)

Table S1 Meteorological conditions during periods and subperiods of the campaign:

28th – 29th June. "PoV N" resulting from a northerly (continental) synoptic circulation on the east side of a high pressure system located on Western Europe. Winds are weak, except for afternoon hours when convective systems develop over the Apennines and the Alps.
30th June – 2nd July, "PoV ENE" and the north-eastern circulation is confirmed by wind fields at the top of the PBL (1500 m).Typically local winds are weak at night time and stronger in the afternoon with an easterly component, which is the typical summer circulation in this sector of the Po Valley. On 2nd July, large convective systems develops over the eastern Po Valley without hitting SPC (but the station was influenced by the wind fields generated by the storms). The circulation on this day cannot be captured by the back trajectories.
2nd-4th July. "PoV WNW", which reflect an intensification of winds from the inner Po Valley (WNW), although wind direction was quite variable in this period. The afternoon convection decreases with (apparently) a reduced ventilation of the Po Valley, causing a progressive warming (higher Tmax) at the ground, and accumulation of pollutants (as seen by the Lidar). The warming in the lower levels brings instability with increasing CAPE (convective available potential energy) with a maximum on 4th July. This leads to the big storm on the night of the 4th-5th.
5th July, Strong precipitation event in the night and the air is considerably cleaned up during the day.
6th – 7th July, "PoV WNW", but this is not confirmed by the analysis of local winds and of satellite pictures, which show instead a W/SW circulation (from Ligurian Sea and Apennines). This is captured by backtrajectories only in the afternoon of 7th July, More cloudy. Precipitating systems travelling eastward over the Po Valley on 7th July hit SPC.
8th – 9th (until midday) July, "West1" or "West2" and westerly winds recorded by ground sensors and radio soundings at all heights, Clear sky or with scattered clouds.
9th (afternoon) – 11th July, Lowest Tmax of the campaign, progressive decrease of Tmin, more humid. BT types "PoV WNW", but actually the circulation is complex: westerlies persist at the top of the PBL (1500 m asl), and easterly winds (from the Adriatic) intensify at ground level at the end of this period, especially on 11th July. Precipitating systems developing on the Apennines on 9th July around midday and bringing a lot of rain in Bologna, then in SPC. On 10th July, precipitating systems in the eastern Po Valley with heavy rain in SPC. It is impossible to capture the impact of such convective systems on air mass history during these days.
12th July, Lowest Tmin of the campaign. "PoV ENE" with easterly winds confirmed by ground measurements, whereas westerlies persists at the top of the mixing layer (1500 m asl).

Table S2 summary of the HR-ToF-AMS PMF results with varying the number of factors

Number of Factors	**Factors**	**Note**
2	HOA/OOA	General HOA and OOA factors, mixed together
3	HOA/OOA/SV-OOA	Large residuals at key m/z's and time periods.
4	HOA/SV-OOA/LV-OOA-LO/LV-OOA-MO	LV-OOA-LO/LV-OOA-MO are split, showing with different time trends.
5	HOA/SV-OOA/LV-OOA-LO/LV-OOA-MO/COA	A new factor COA is found. Distinctive diurnal cycles for the factors, and mass spectra that compare well with database MS. Better correlation with concomitant measurements than with the four factor solution (increase average R^2). Factors LV-OOA-LO and LV-OOA-MO are very conservative (R^2>0.98) relative to the four factor solution. The new factor COA comes mainly from SV-OOA and partially from HOA. The new COA factor is supported by external measurements (NMR, ATOFMS).
>5	Splitting	HOA and the single LV-OOAs begin to split

Table S3 Correlations (r^2 > 0.3) of TAG PMF factors with AMS chemical species, AMS PMF factors, ATOFMS clusters, and PSAP BC during short focus period (7-11 of July).

HR-ToFMS-TAG PMF Factors	HR-ToF-AMS OM	HR-ToF-AMS NO^-_3	HR-ToF-AMS $SO^=_4$	HR-ToF-AMS NH^+_4	HR-ToF-AMS Cl^-	HR-ToF-AMS LV-OOA-MO	HR-ToF-AMS LV-OOA-LO	HR-ToF-AMS SV-OOA	HR-ToF-AMS HOA	HR-ToF-AMS COA	ATOFMS NIT-Reg	ATOFMS NIT-Loc	ATOFMS EC-Reg	ATOFMS SUL-Reg	ATFOMS K-CN-Amine	ATFOMS NIT-Loc/Reg	ATFOMS OC-NIT-SUL	ATFOMS NaCl	PSAP BC
Alkanes	0.50	0.61	-	0.60	-	-	0.51	0.39	**0.54**	-	**0.82**	0.49	**0.69**	-	-	-	-	-	**0.61**
Alkanes UCM	0.44	0.57	-	0.54	-	-	-	0.43	**0.54**	-	**0.84**	0.64	**0.77**	-	0.44	0.35	0.36	-	**0.69**
Alkanes (combined)	0.48	0.61	-	0.59	-	-	0.40	0.43	**0.56**	-	**0.86**	0.60	**0.76**	-	0.39	0.32	0.31	-	**0.68**
Monocarboxylic acid	-	-	-	-	-	-	-	-	0.33	-	0.43	-	-	-	-	-	-	-	0.31
Monocarboxylic acid 2	0.53	0.45	-	0.43	0.35	-	0.37	0.49	0.44	**0.51**	0.36	0.45	-	-	0.32	-	0.48	-	0.43
Monocarboxylic acid (combined)	0.52	0.43	-	0.42	0.31	-	0.33	0.46	0.46	**0.49**	0.43	0.46	-	-	0.32	-	0.43	-	0.45
Organic Nitrogen 1	-	-	-	-	-	**0.53**	-	-	-	-	-	-	-	-	-	-	-	-	-
Organic Nitrogen 2	0.55	0.61	-	0.60	-	-	0.45	0.48	0.49	0.37	0.69	0.67	0.50	-	-	0.45	0.41	-	0.60
Organic Nitrogen (combined)	0.45	0.56	-	0.55	-	-	0.47	0.35	0.35	-	0.66	0.62	0.51	-	-	0.44	0.30	-	0.50
Benzoic acid	-	-	-	-	-	**0.39**	-	-	-	-	-	-	-	-	-	-	-	-	-
Sulfate /Organosulfate	0.35	0.39	-	0.39	-	-	-	0.32	-	-	-	-	-	-	-	-	-	-	-
Chlorine-Containing	0.39	0.55	-	0.54	-	-	-	0.39	0.39	-	0.60	0.58	0.57	-	-	-	-	-	0.49
Unknown 1	-	-	-	-	-	-	-	-	-	-	0.52	-	0.43	-	-	-	-	-	-
Unknown 2	0.35	0.41	-	0.38	-	-	-	0.31	0.42	-	0.61	0.56	0.44	-	-	-	-	-	0.50
Unknown 3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown 4	-	-	-	-	-	-	-	-	-	-	0.38	-	0.39	-	-	-	-	-	-
Unknown decomposition 1	-	0.37	-	0.39	-	-	0.34	-	-	-	0.50	-	0.44	-	-	-	-	-	-
Unknown decomposition 2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown decomposition 3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Unknown decomposition 4	0.35	0.46	-	0.45	-	-	0.37	-	0.33	-	0.68	0.59	0.51	-	0.31	0.39	-	-	0.50
Unknown decomposition 5	-	-	-	-	-	0.34	0.32	-	-	-	-	-	-	-	-	-	-	-	-
Unknown decomposition 6	0.46	0.52	-	0.52	-	-	0.52	0.35	0.30	-	0.52	0.49	0.43	-	-	0.46	0.31	-	0.42
Column bleed	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

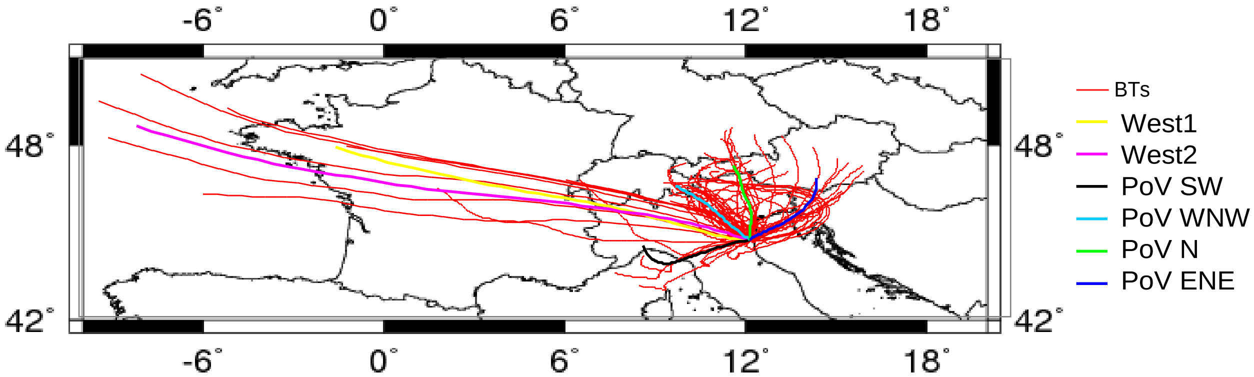


Figure S1. Back-trajectories (BTs) and their main clusters. "PoV" (Po Valley) air masses reached the station prevalently from SW, WNW, N or ENE. Longer, westerly air masses (West1 and 2) characterized the days between 8th and 9th July.

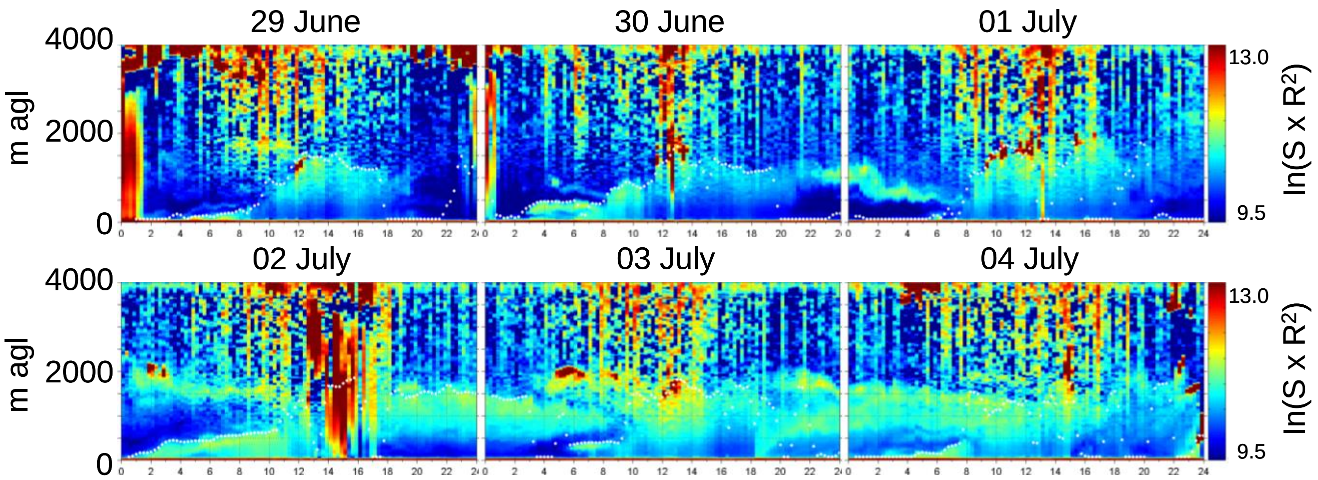


Figure S2. Ceilometer data from 29 June to 4 July. Strong extinction bands reaching the ground on 29 June at 01 AM and on 2 July at 03 PM are due to rain events.

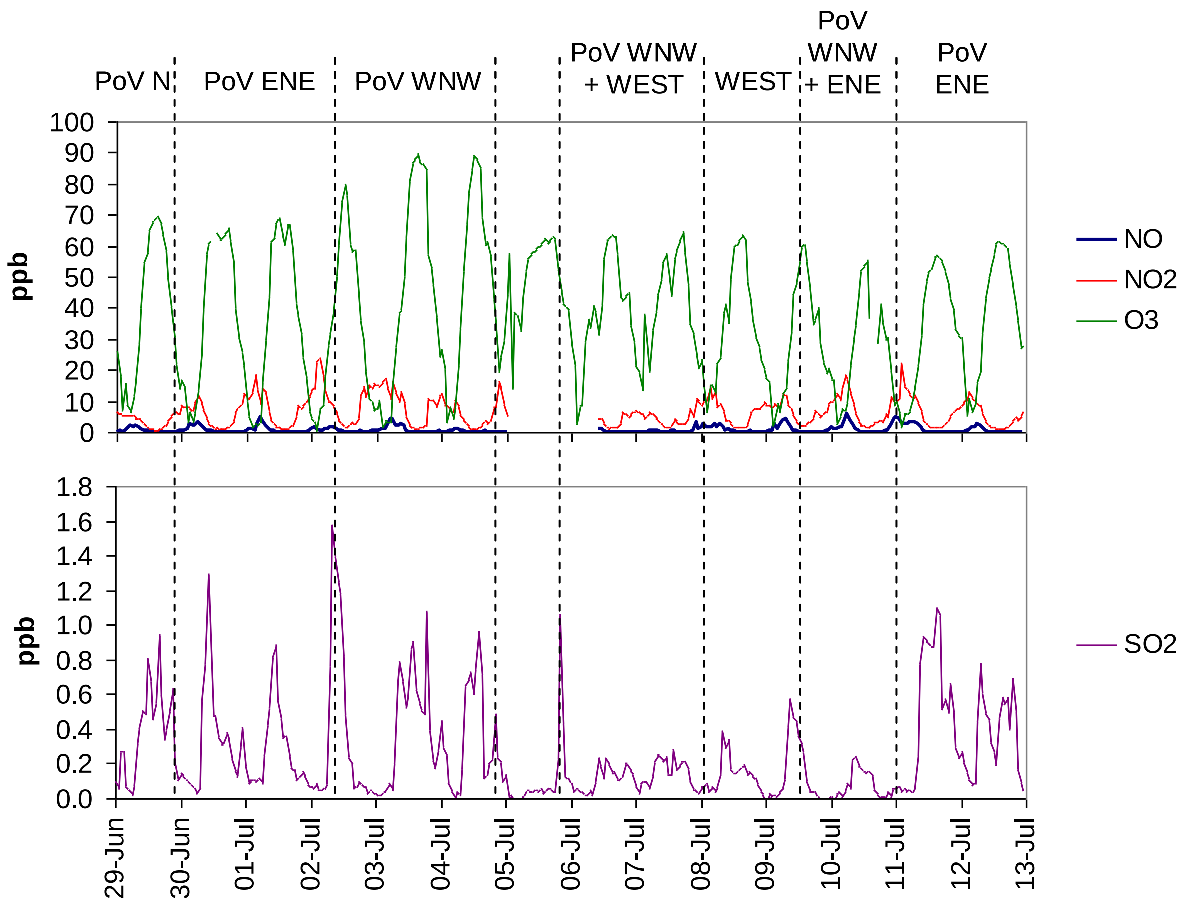


Figure S3. Time trends (hourly averages) of the concentrations of ozone, nitrogen oxides and SO_2 during the campaign.

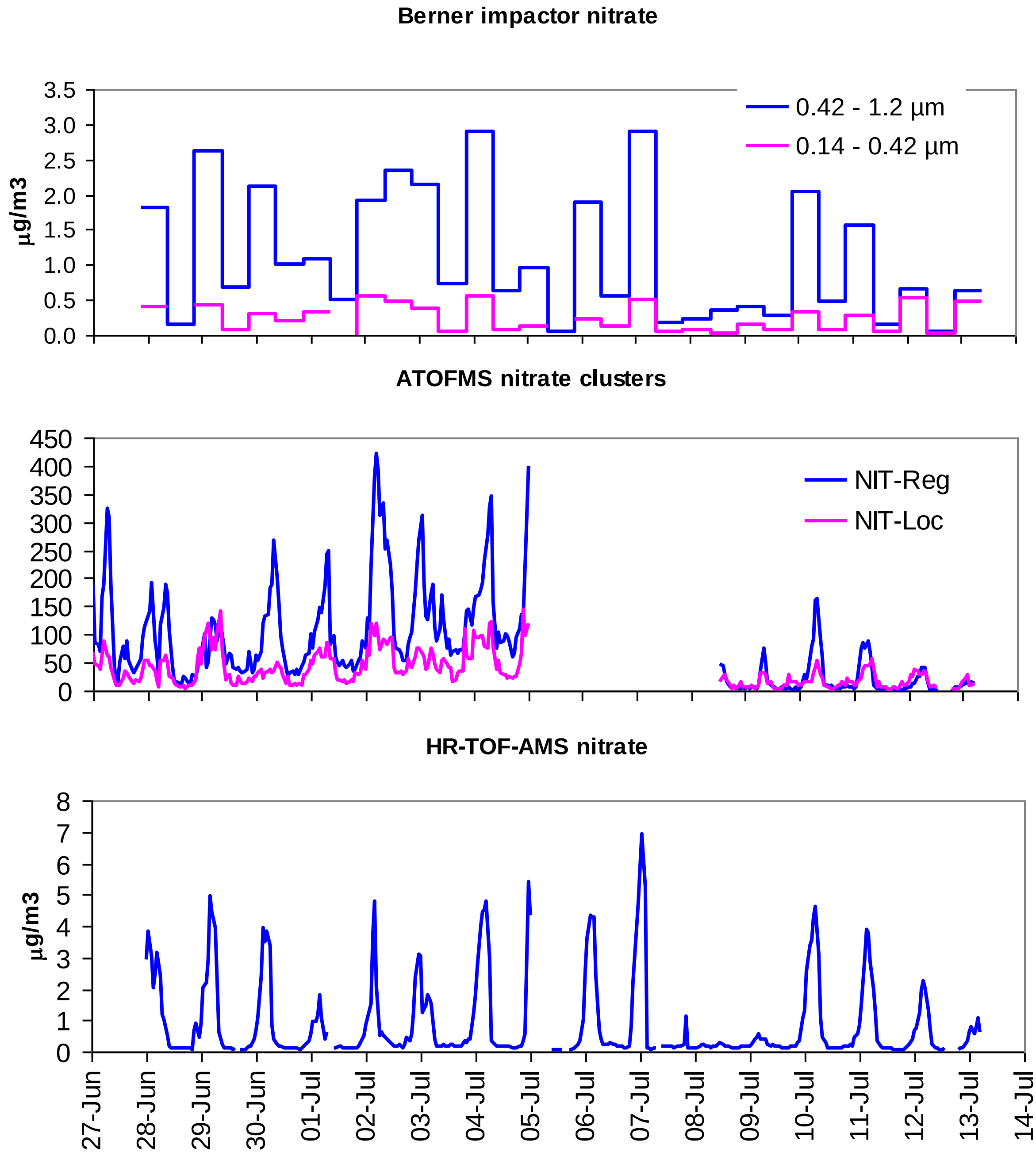
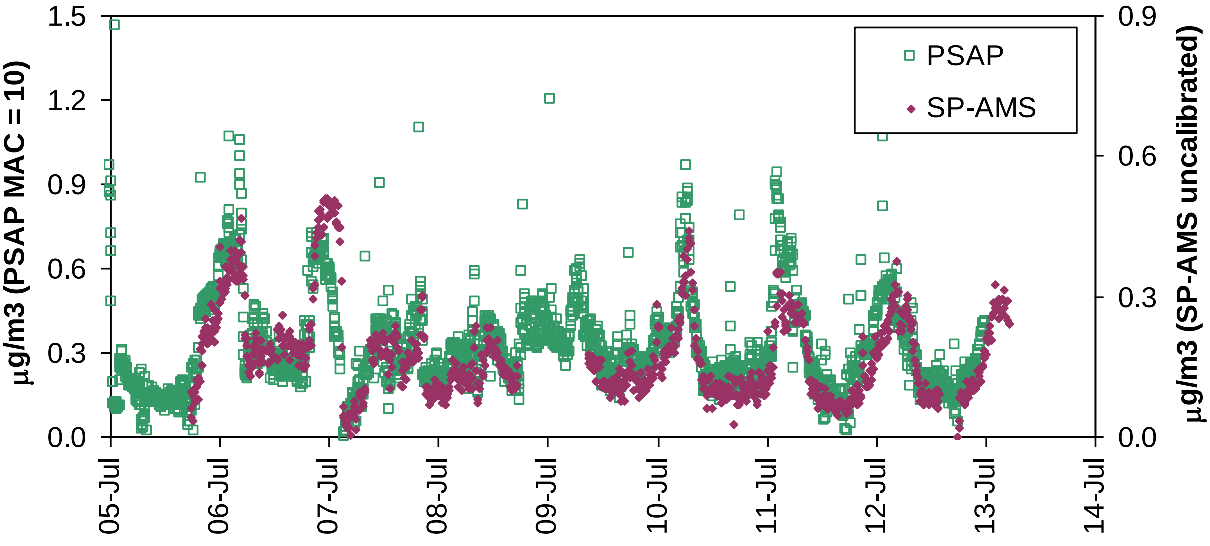
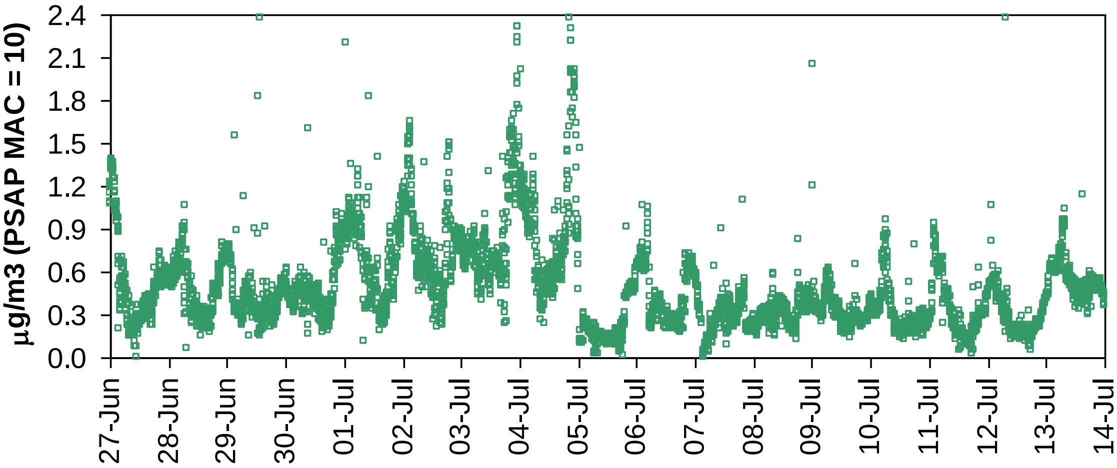


Figure S4. Nitrate concentrations in the accumulation mode from Berner impactors, ATOFMS and HR-ToF-AMS.



a)



b)

Figure S5.a) Comparison between PSAP and SP-AMS measurements of BC, b) full BC record from PSAP.

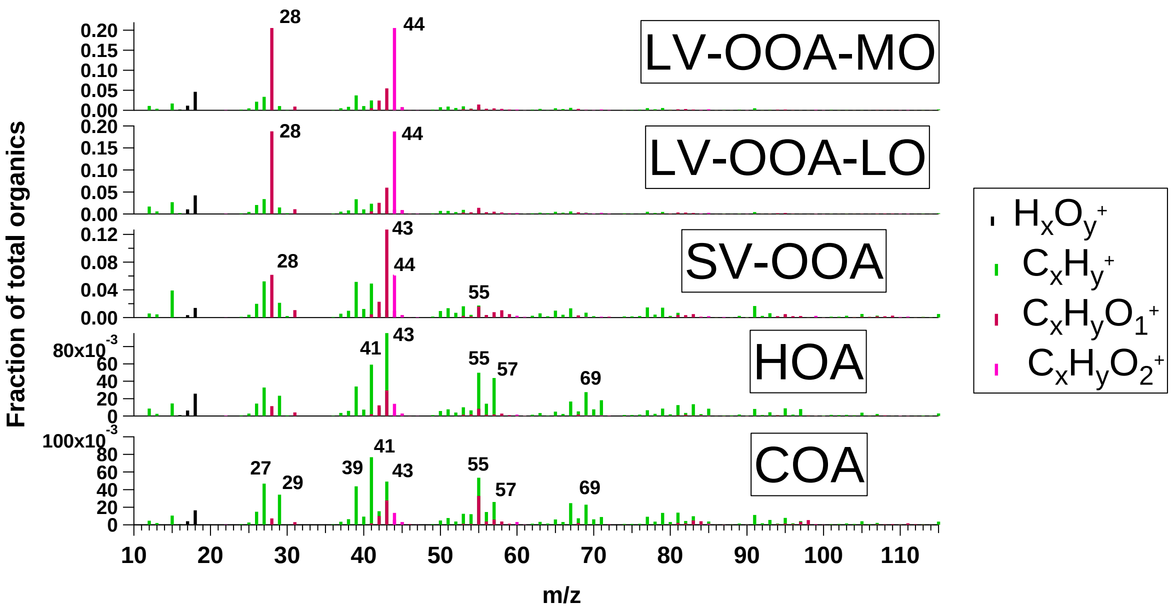


Figure S6. HR-ToF-AMS spectra of aerosol organic matter for the four factors from PMF.

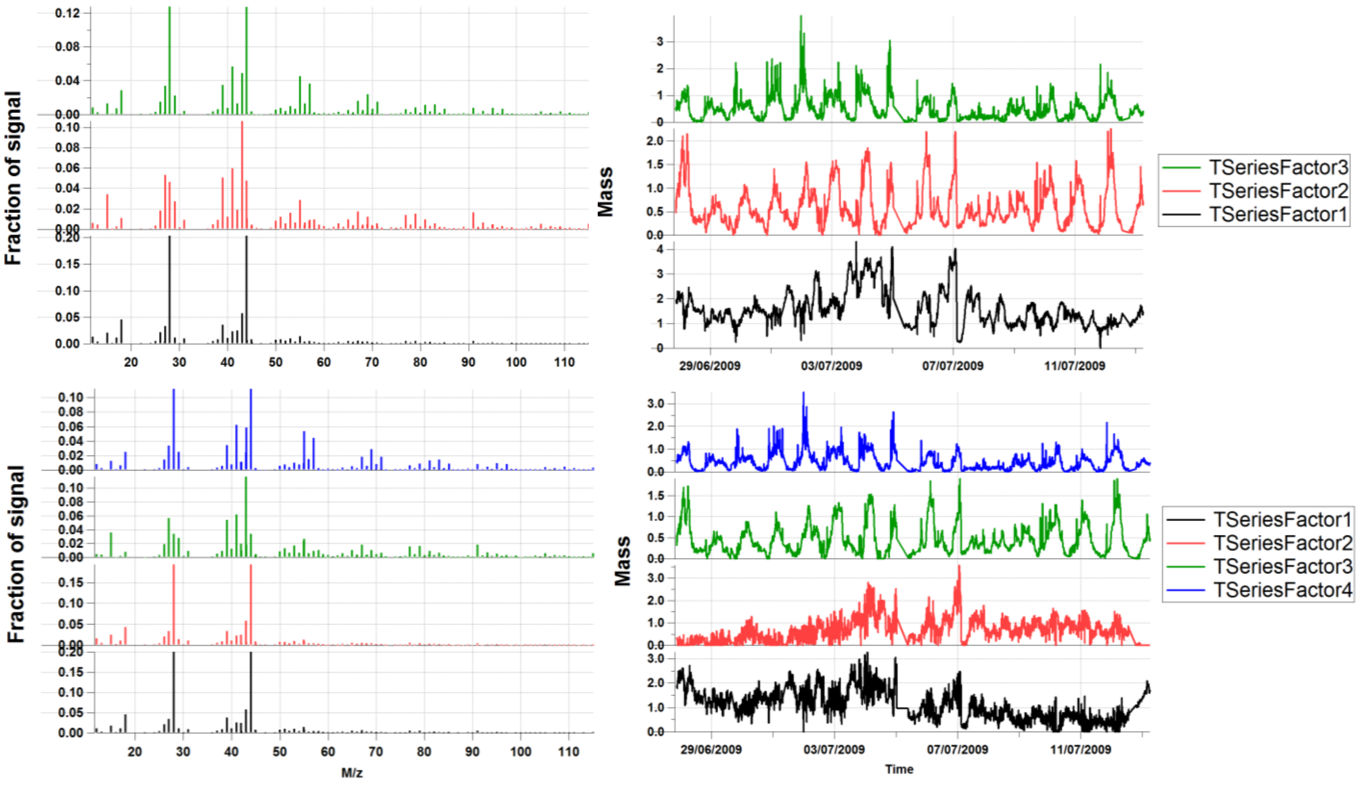
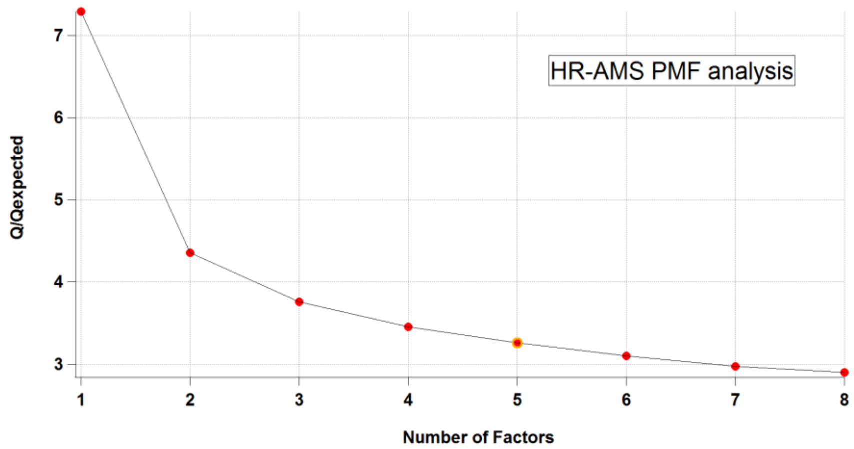
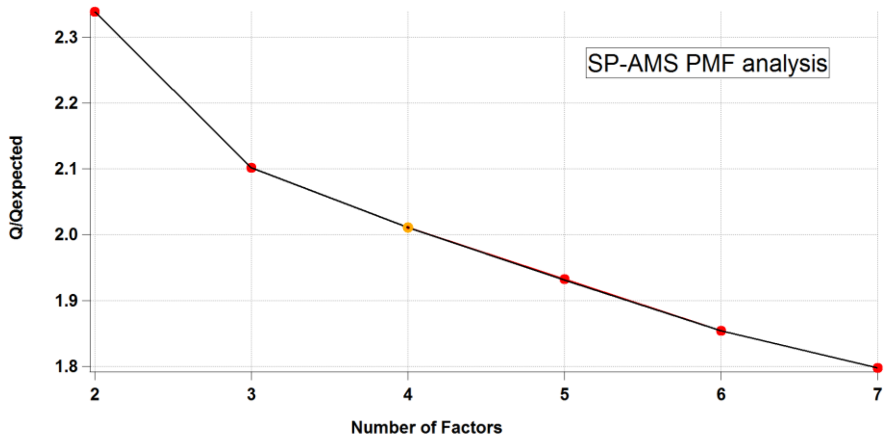


Figure S7. HR-Tof-AMS PMF factors mass spectra (left) and time series (right) for a three factors (top) and four factors (bottom) solutions. The mass concentration unit in the time series is µg/m^3. Notice that the divide between LV-OOA-LO and LV-OOA-MO occurs early in the PMF analysis when the number of factors is progressively increased. By adopting a four-factor solution, when the COA is still undifferentiated (compare with Fig. 9 in the main text), PMF already distinguishes between LV-OOA-MO and LV-OOA-LO. Increasing factor number from four to five does not perturb the contributions and the spectral profiles of the two LV-OOA types.

a)



b)



c)

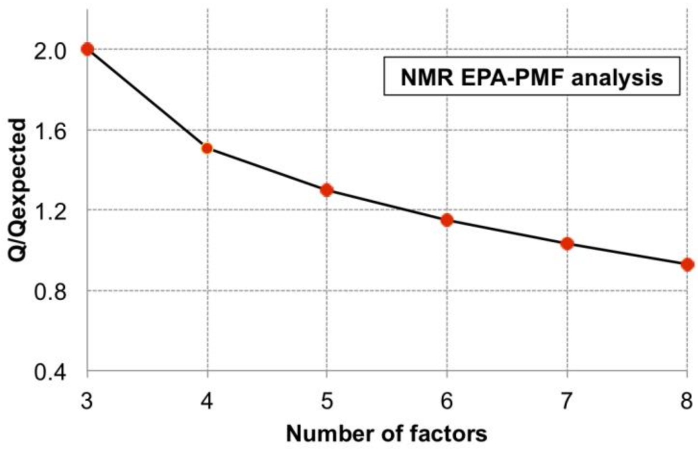


Figure S8. Q/Qexpected versus the number of factors for PMF factor analysis carried out on the a) HR-ToF-AMS, b) SP-AMS, and c) NMR datasets.

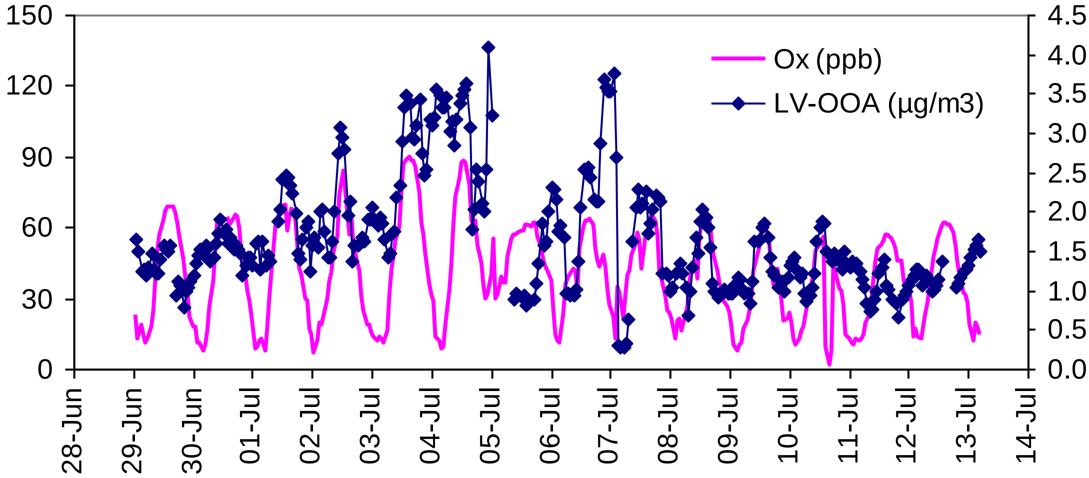


Figure S9. Time trends of odd oxygen (Ox) and total LV-OOA (MO+LO).

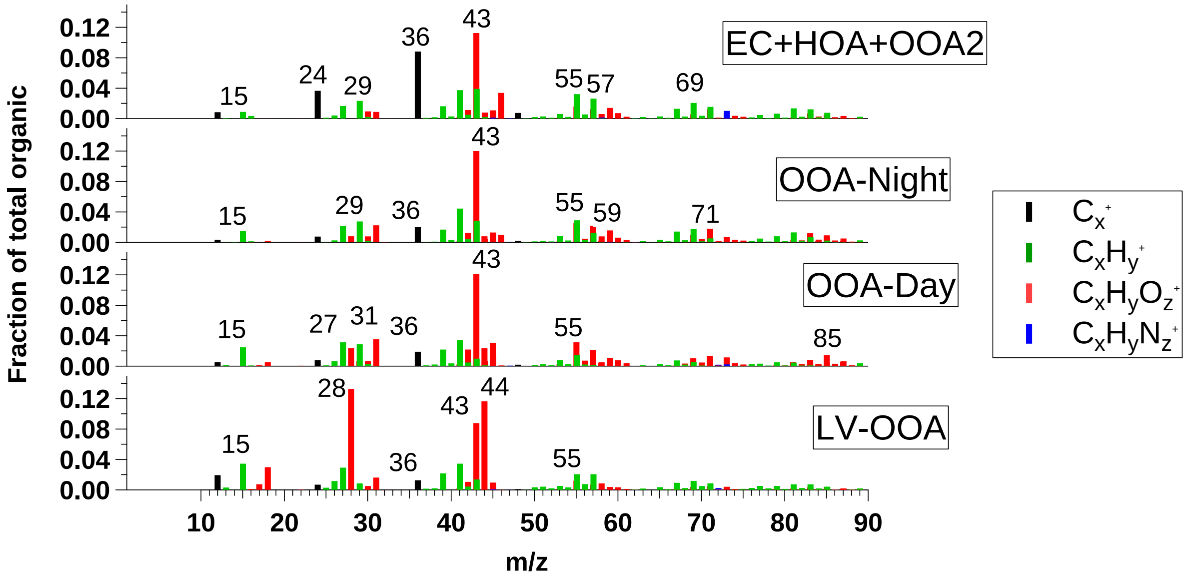


Figure S10. SP-AMS PMF spectral profiles (5 factor solution).

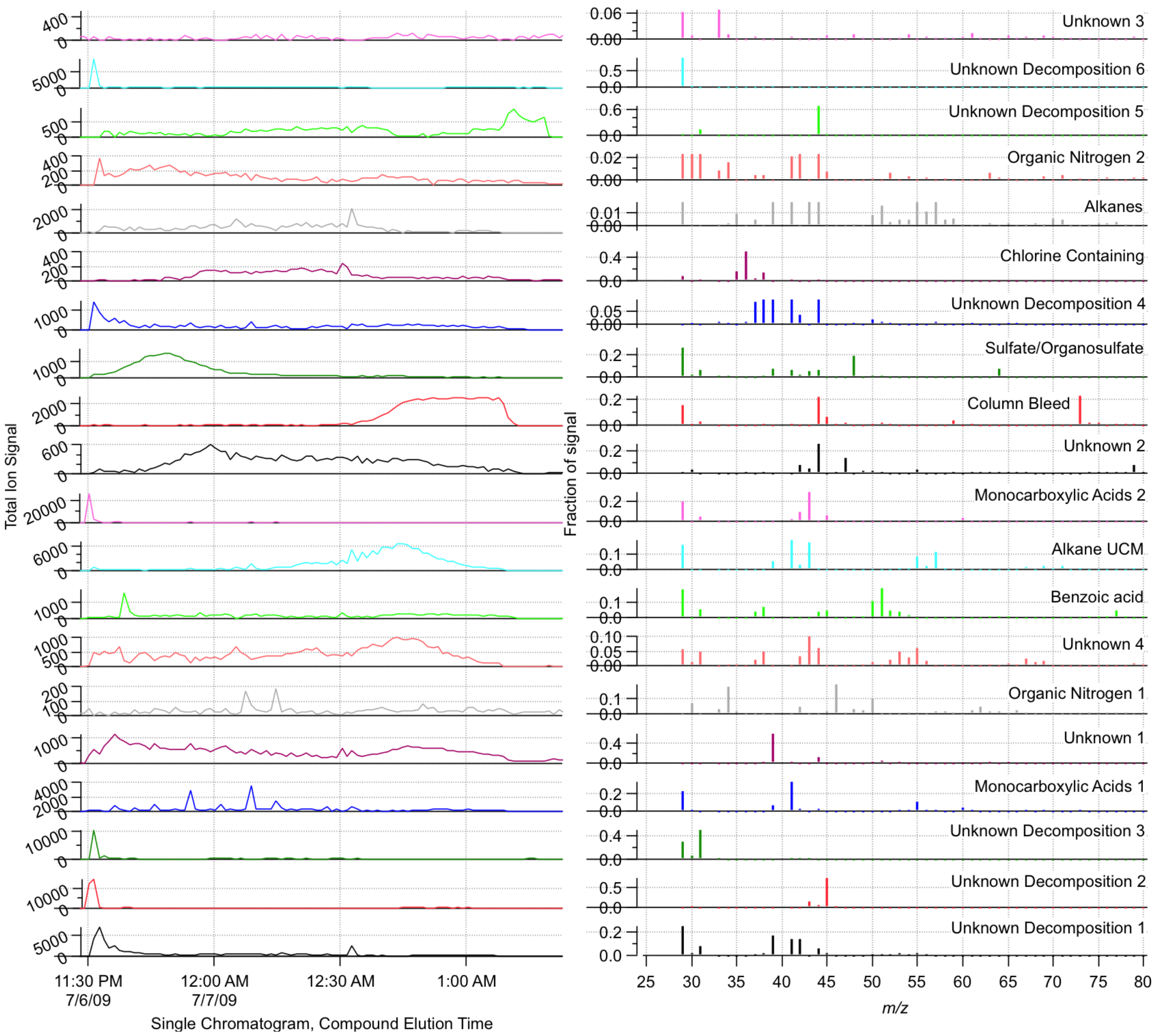


Figure S11. 20-factor PMF solution from the HR-ToFMS-TAG. Time-series on the left represents just a single sample and it can be seen how this PMF technique separates the components of a chromatogram. Factor profiles (average mass spectra) are shown on the right. Many factors are identified as a series of compounds (e.g., alkanes, acids), or even just a single compound (i.e., benzoic acid). Other factors are unidentified and several are a result of thermal decomposition during sample delivery via thermal desorption onto the column (seen at the very start of the chromatogram, prior to GC heating). The high pass band filter was under development during deployment and operated with a restricted band pass, resulting in mass spectra that had high response to small ions and low response to large ions when compared to a standard mass spectral reference library (e.g., NIST/EPA/NIH Mass Spectral Library).

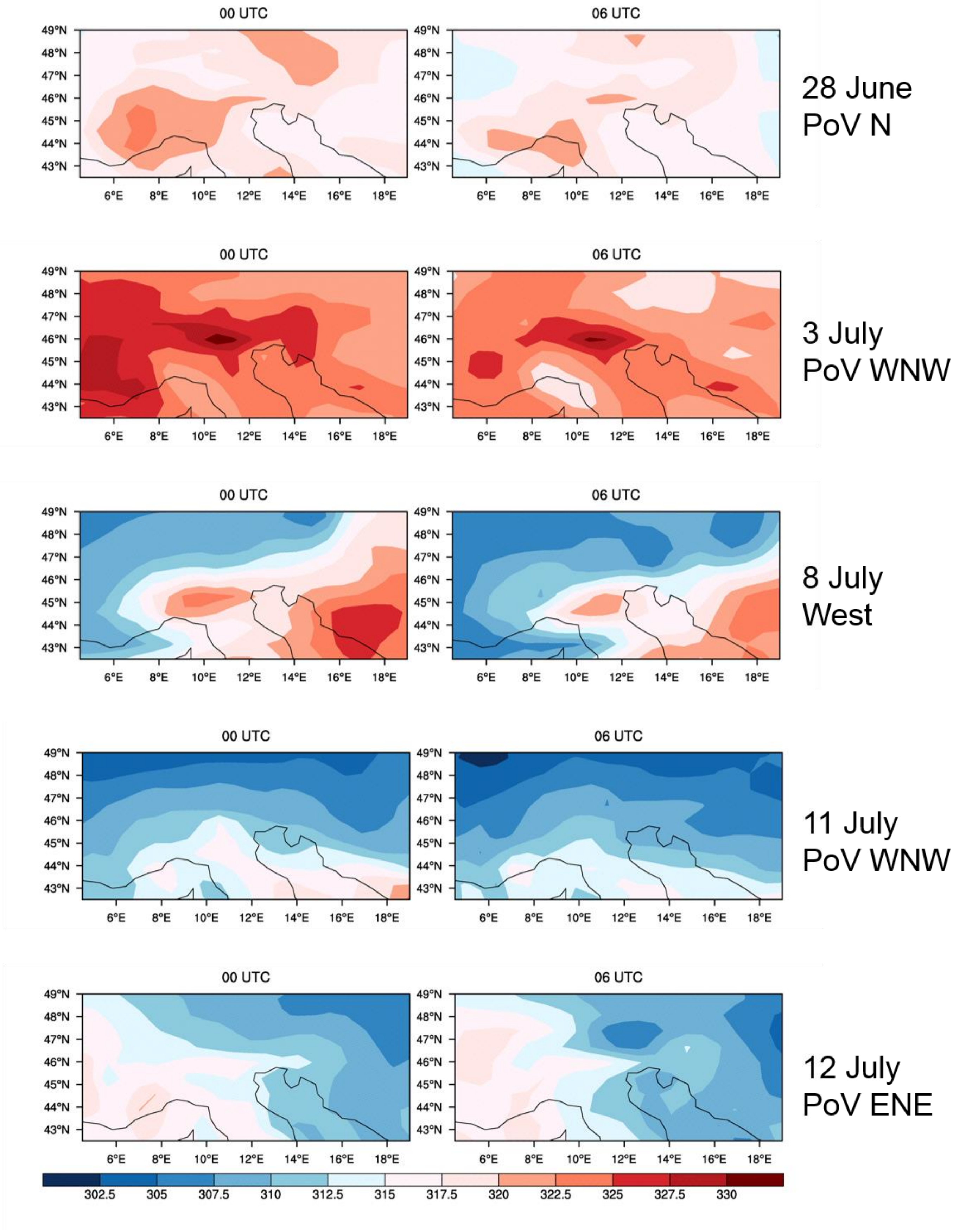


Figure S12. Equivalent potential temperature (K) at 850 hPa maps for north Italy and the great alpine region from ERA-interim for 28 June, 3, 8, 11 and 12 July at 00:00 UTC (left column) and 06:00 UTC (right). Prevalent air mass type on each day is shown on the right.