acp-2018-297: “Driving parameters of biogenic volatile organic compounds and consequences on new particle formation observed at an Eastern Mediterranean background site”

The presented manuscript describes the on-line and off-line measurements of various organic compounds at a remote Mediterranean measurement site. The measurements include 20 days of data. The authors present characteristics of 4 different NPF classes, which they categorized based on air mass origin. The manuscript presents very interesting new results. I suggest minor revisions, described in the following.

Authors’ Responses to Referee #2

We would like to thank the Referee #2 for her/his general feedback and each of her/his useful comments/questions for improving the quality of this manuscript. All comments addressed by both referees have been taken into account in the revised version of the manuscript. In this respect, several figures were notably modified and included in the supplementary. Please note that figures numbers are now different in this new version.

In the present document, authors’ answers to the specific comments addressed by Referee #2 are mentioned in **blue**, while changes made into the revised manuscript are shown in **green**.

The comments on the manuscript are listed as follows:

1/ About the writing style of the manuscript, there are quite a lot of grammatical mistakes in the manuscript and it is very difficult to read. I suggest asking a native English speaker to correct the language before re-submitting.

The revised manuscript was corrected by a native English speaker. The referee #2 is invited to look at the peer review version of the revised manuscript in order to see all the modifications made consequently to his/her comment.

2/ Why are you not showing any data from the NAIS measurements? It would be very interesting to see mean diel cycles for different size classes below 20 nm from the NAIS measurements for different NPF event day classes and non-event days. A comparison to PSM size classes and DMPS would be helpful in the same figures.

In this study, daily size distribution spectra measured with NAIS were mainly used to strengthen the identification and the classification of NPF events. In fact, the authors followed the classification scheme of Yli-Juuti et al. (2009), combining visual observation of NPF events from (N)AIS and DMPS measurements. The evolution of particle size distributions also gives us a way to know their growth and nucleation rates.

Additionally, during the intensive field campaign, the PSM was not operated in the scan mode (for the measurement of all particles having a diameter between 1 and 2.5 nm) but in the total mode (for the measurement of all particles larger than 1 nm), which did not allow any growth and nucleation rate calculation in the size range 1-3 nm.

As mentioned by referee #2, there are already numerous Figures containing many information that's why the authors prefer not showing NAIS mean diel cycles in this study. Moreover, the aim of this study is not to provide an extensive investigation of NPF events but rather to focus on the role of BVOCs in the early stages of formation and the growth of atmospheric aerosol particles.

In the preliminary study, each DMPS size class was investigated individually. During NPF events, number concentrations of larger size particle classes can increase with a delay compared to number concentrations of first particle size class (20-27 nm from 8 to 11 March and 10-13 nm from 12 to 27 March). An example is provided in Figure X1, in agreement with the banana-shape depicted in Figure 8 of the manuscript.

Furthermore, to summarize the results and according to the aim of this study, the authors only made the distinction between $N_{PSM\text{-}DMPS}$, corresponding to number concentrations of sub-20 nm particles (from 8 to 11 March) or sub-10 nm particles (from 12 to 27 March) and N_{DMPS}, corresponding to number concentrations of either 20-200 nm particles (from 8 to 11 March) or 10-250 nm particles (from 12 to 27 March) in the manuscript. These two parameters can provide information on the early stages of formation (regarding $N_{PSM\text{-}DMPS}$) and the growth (N_{DMPS}) of atmospheric aerosol particles. As a result, N_{PSM} was decomposed into N_{DMPS} and $N_{PSM\text{-}DMPS}$ in Figure 9 of the revised manuscript (see authors' response 9). The authors hope that Figure 9 of the revised manuscript will meet referee #2 expectations about comparisons of PSM and DMPS measurements in the same Figures.

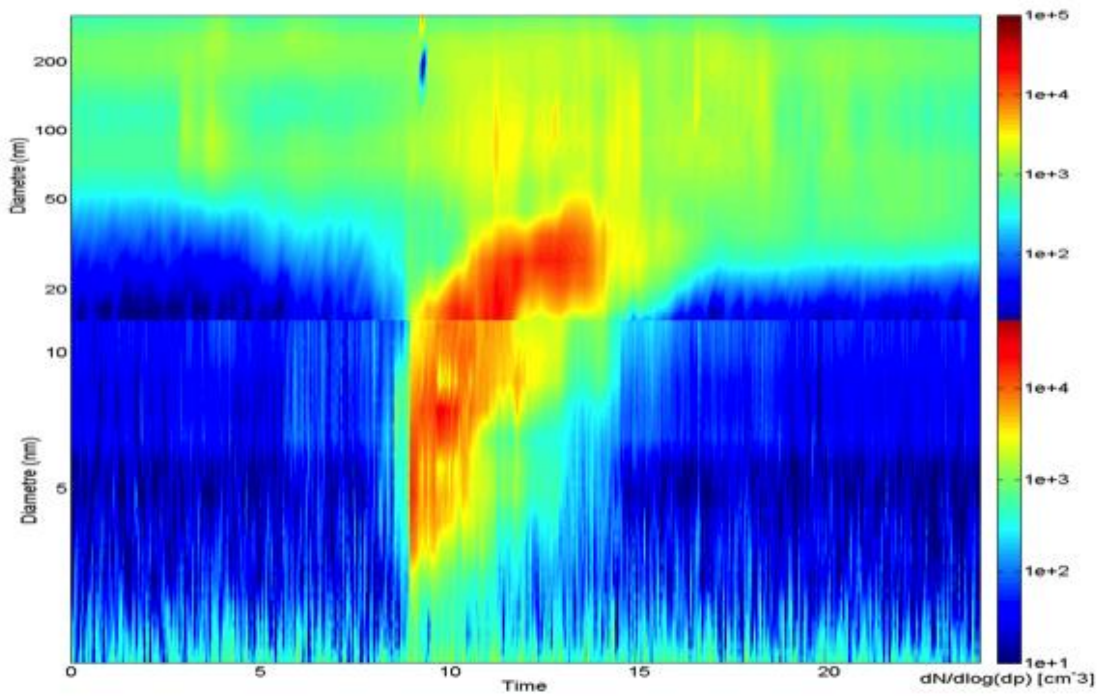


Figure 8: Example of size distribution spectra, measured with DMPS and NAIS, showing an NPF event of type Ia occurring on 14 March 2015 at the CAO station

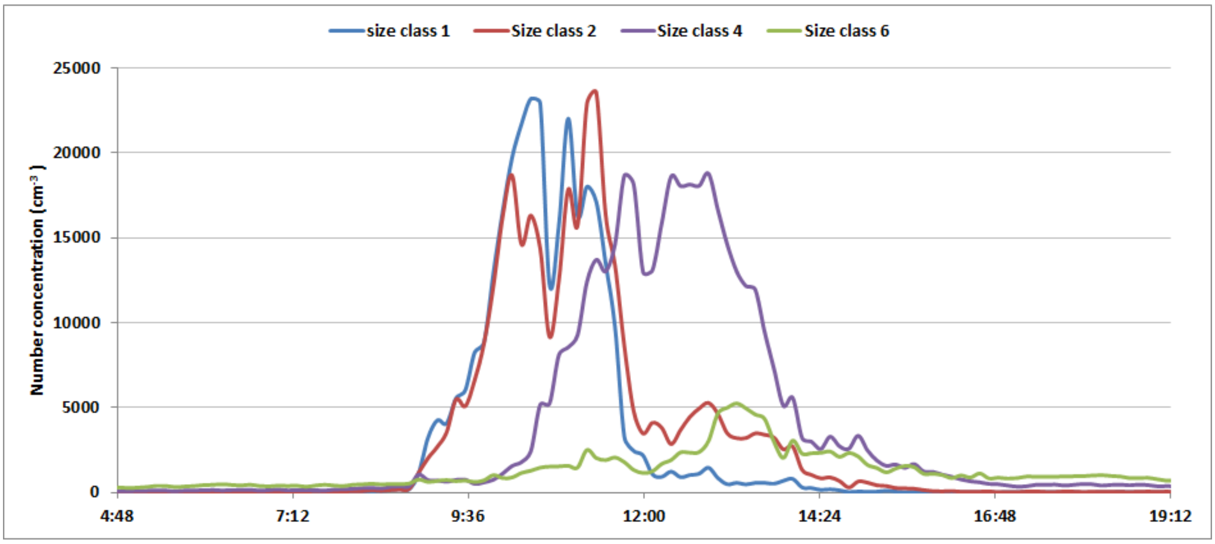


Figure X1: Time series of a selection of number concentrations, measured with the DMPS, showing an NPF event of type Ia occurring on 14 March 2015 at the CAO station

3/ A table, summarizing the findings regarding NPF event days and non-event days is needed. That table could contain the information that is shown in Figures 10 and 11, for the different NPF classes found in your analysis.

As proposed by referee #2, Figure 10 (of the initial version of the manuscript) was removed and converted into a table (as Table 2 in the revised manuscript) showing mean and standard deviation values for atmospheric parameters (supporting the classification of event days) along with property indicators for NPF events and factors with suspected influence on nucleation events.

Otherwise, Figure 11 was kept, and hence not integrated to Table 2, since the importance of diurnal variations as point out by referee #2 (please see authors' response 9 in complement). Nevertheless, mean and standard deviation values for some meteorological parameters (temperature, relative humidity and solar radiation) were added to Table 2 of the revised manuscript.

Table 2 of the revised manuscript is the following:

Table 2: Average and standard deviation of CS, particle formation and growth rates ($J_{1.5}$ and $GR_{1.5\text{-}3}$, respectively), meteorological parameters (temperature, relative humidity and solar radiation) and atmospheric parameters daily concentrations measured at the CAO station in case of event (NPF1-NPF4) or non-event days.

Parameter	NPF1 event days	NPF2 event days	NPF3 event days	NPF4 event days	Non-event days
CS (s^{-1})	0.12 ± 0.02	0.09 ± 0.02	0.08 ± 0.01	0.12	0.07 ± 0.04
J_3 ($cm^{-3}s^{-1}$)	5.0	11.4 ± 4.9	6.4 ± 1.4	8.1	-
$GR_{1.5\text{-}3}$ ($nm.h^{-1}$)	5.0	3.7 ± 1.6	1.9 ± 0.6	2.8	-
PM_1 ($\mu g.m^{-3}$)	9.7 ± 1.4	12.9 ± 2.8	5.9 ± 0.7	9.8	6.4 ± 3.6
SO_4 ($\mu g.m^{-3}$)	2.9 ± 0.7	3.3 ± 1.0	1.9 ± 0.3	3.1	1.9 ± 1.3
NH_4 ($\mu g.m^{-3}$)	1.9 ± 0.4	2.1 ± 0.6	1.2 ± 0.2	1.8	1.2 ± 0.8
NO_3 ($\mu g.m^{-3}$)	0.5 ± 0.2	0.7 ± 0.2	0.3 ± 0.1	0.3	0.3 ± 0.1
OM ($\mu g.m^{-3}$)	4.3 ± 0.4	6.8 ± 1.5	2.6 ± 0.3	4.5	2.9 ± 1.5
HOA ($\mu g.m^{-3}$)	0.4 ± 0.1	0.7 ± 0.2	0.3 ± 0.1	0.4	0.3 ± 0.1
SV-OOA ($\mu g.m^{-3}$)	1.3 ± 0.2	2.5 ± 0.9	0.8 ± 0.2	1.1	0.9 ± 0.4
LV-OOA ($\mu g.m^{-3}$)	1.7 ± 0.2	1.8 ± 0.5	1.3 ± 0.1	2.2	1.3 ± 0.7
BC ($\mu g.m^{-3}$)	0.5 ± 0.1	1.0 ± 0.3	0.3 ± 0.1	0.4	0.3 ± 0.1
CO (ppb)	158.2 ± 5.5	162.5 ± 9.2	160.1 ± 19.5	155.1	151.6 ± 13.2
NO_2 (ppb)	1.1 ± 0.2	1.4 ± 0.5	0.8 ± 0.1	0.7	0.6 ± 0.2
SO_2 (ppb)	0.7 ± 0.3	0.7 ± 0.3	0.3 ± 0.1	0.2	0.2 ± 0.1
H_2SO_4 ($molec.cm^{-3}$)	$6.3\ 10^7 \pm 5.2\ 10^7$	$1.4\ 10^8 \pm 8.4\ 10^7$	$4.3\ 10^7 \pm 1.8\ 10^7$	$1.8\ 10^7$	$2.3\ 10^7 \pm 1.7\ 10^7$
Isoprene (ppt)	34 ± 7	79 ± 29	33 ± 7	57	47 ± 16
MVK+MACR (ppt)	27 ± 4	61 ± 23	25 ± 1	26	30 ± 8
Monoterpenes (ppt)	115 ± 19	361 ± 209	148 ± 80	130	306 ± 204
O_3 (ppb)	50.4 ± 3.7	48.2 ± 2.8	46.4 ± 2.6	48.2	46.5 ± 4.3
Temperature (°C)	14.2 ± 2.4	15.4 ± 3.7	11.8 ± 2.4	10.7	11.2 ± 1.7
Relative Humidity (%)	54.0 ± 12.3	63.5 ± 18.1	61.3 ± 9.6	63.8	79.6 ± 12.5
Solar radiation ($W.m^{-2}$)	258 ± 213	255 ± 192	305 ± 228	283	203 ± 199

4/ The presented Figures are extensive and contain a lot of information. Please do not use yellow in your Figures, it is very hard to read the content of the Figures if there are yellow lines.

An effort was realized to limit the use of yellow/light orange colors in the Figures of the manuscript. As a consequence, the color used to represent NPF event days categorized by a mixed (anthropogenic/biogenic) influence is now a dark orange (instead of yellow) in order to stay consistent with colors used for NPF event days of individual origin (i.e. red for NPF1 event days of anthropogenic origin and green for NPF3 event days of biogenic origin). The orange color used to represent solar radiation and NH_4 data has been darkened and H_2SO_4 concentrations are now represented in violet (instead of light orange).

The modifications applied to Figures 5, 9, 10 and 11 (of the initial version of manuscript) are explicit in the following answers.

5/ It is sometimes difficult to extract all the information in the Figures. I will make some detailed suggestions in the following.

The authors thank referee #2 for these detailed suggestions which the authors will take into account in the following.

6/ In Figure 4, it is not clear to me, what exactly is presented here? Do those Figures include all measurement days, NPF event days only or non-event days only? Please do not use yellow.

In Figure 4 is presented diurnal variations of isoprene and monoterpenes concentrations. These diurnal variations are also compared with mean diel variations of meteorological parameters (temperature and solar radiation) which are known to influence BVOC emissions, and so indirectly BVOC concentration variations.

This figure includes all BVOC measurement days with a PTR-MS, i.e. from 1 March to 29 March 2015, which has been specified in the caption of Figure 4. This period includes NPF event days and non-event days as the variation of BVOC concentrations was independent of this element.

As suggest by referee #2, the orange color used to represent solar radiation data has been darkened.

Revised Figure 4 is the following:

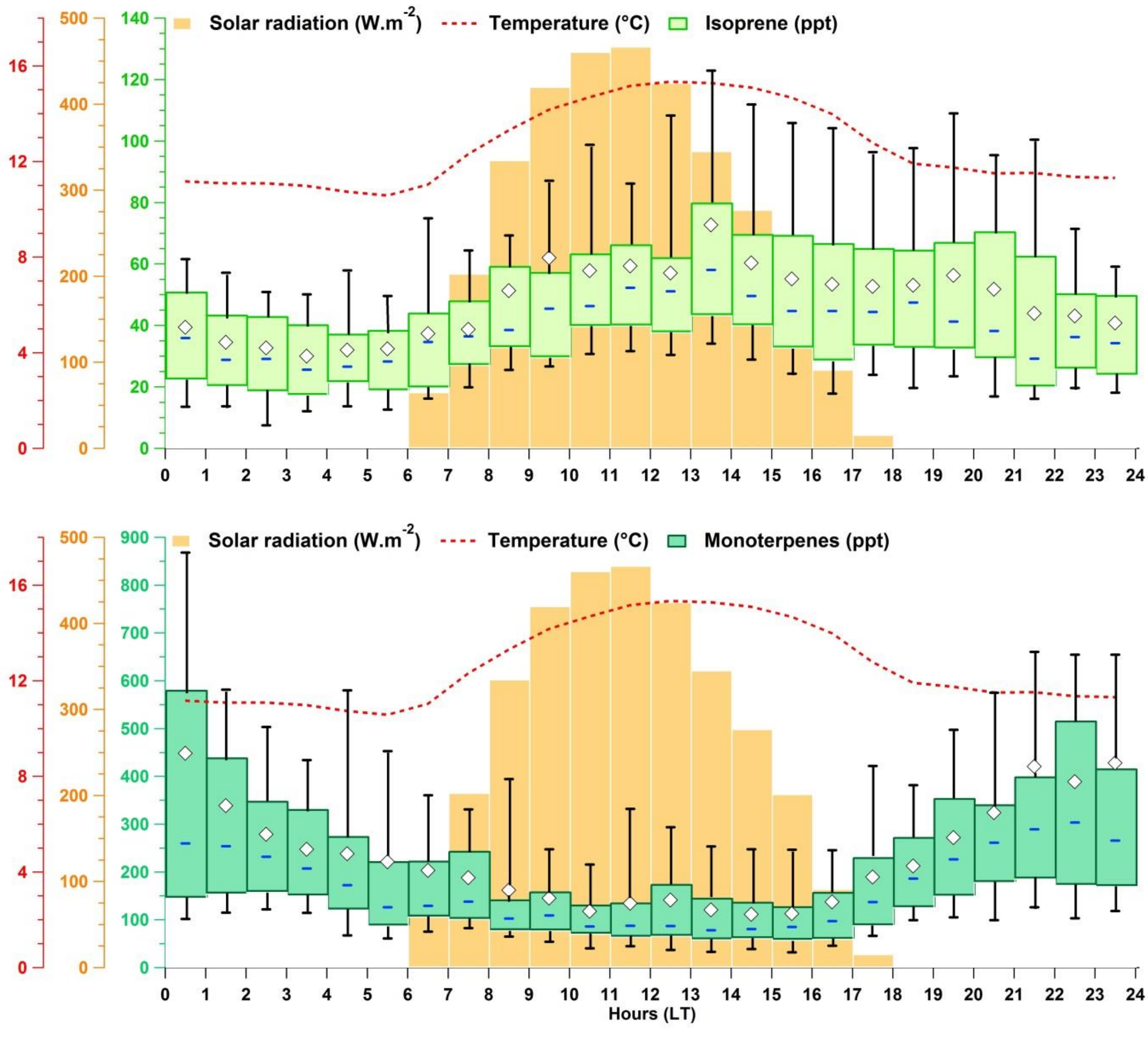


Figure 4: Diel variation of isoprene and monoterpenes, represented by hourly box plots (in green colors) in comparison with mean diel variation of meteorological parameters (solar radiation, temperature displayed as red lines and orange boxes, respectively). This figure includes all BVOC measurement days with a PTR-MS (i.e. from 1 to 29 March 2015). White marker represents the mean value, blue solid line represents the median value and the green box shows the InterQuartile Range (IQR). 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 the first and the ninth deciles (i.e. D1 and D9). Time is given in local time (UTC + 2 h).

7/ Figure 5 is very difficult to read, there is yellow on yellow and an extensive amount of information. I suggest making mean diel cycle Figures, summarizing the different NPF event day classes you observed, showing the same parameters as in each panel of the current Figure.

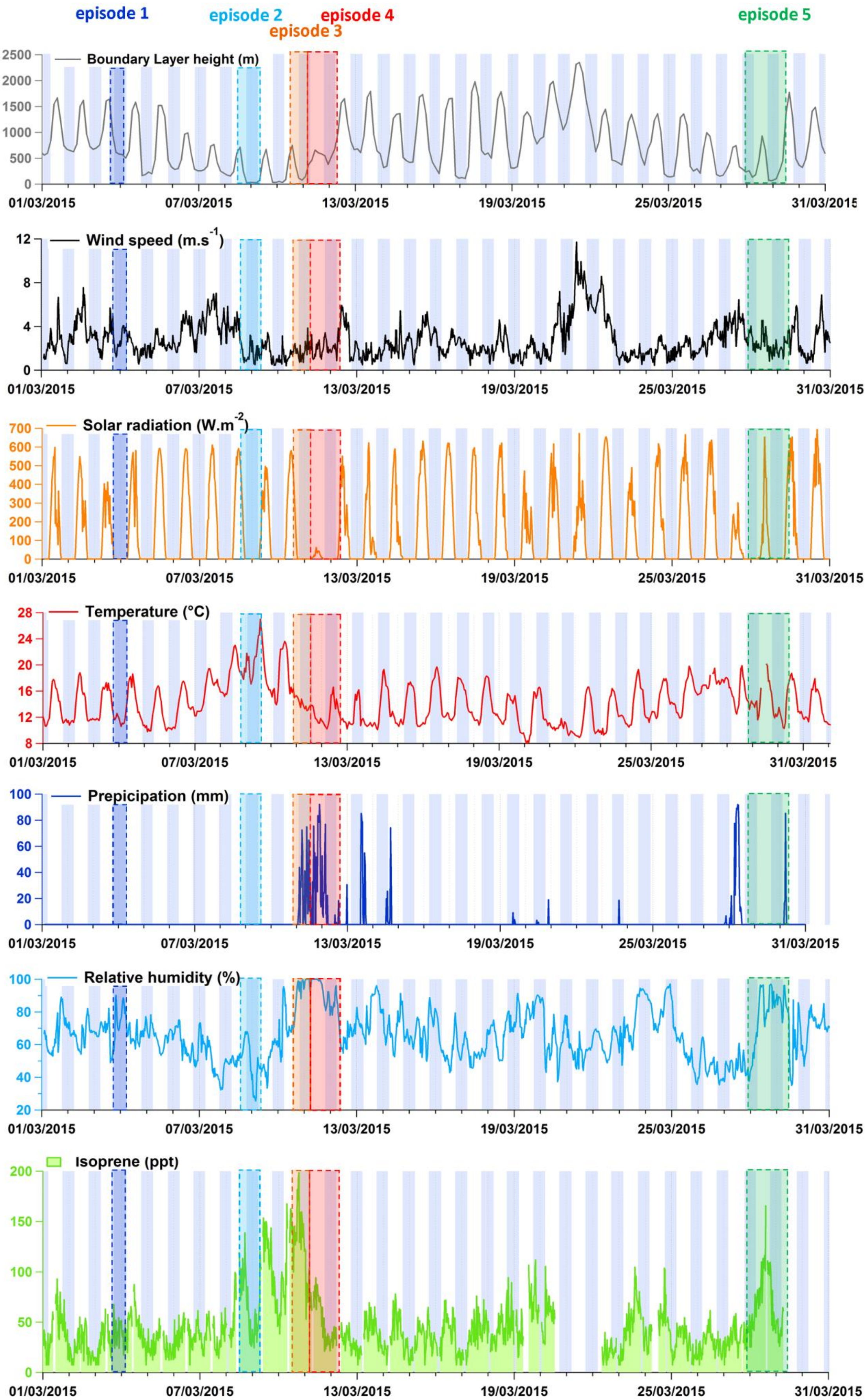
In Figure 5 is presented times variations of main monoterpenes and isoprene examined along with meteorological parameters in order to determine the dominant drivers for variations of BVOC concentrations.

Given the extensive amount of information for the Figure 5, the investigation of meteorological parameter effects on BVOC concentrations was mainly based on the study of 5 specific periods among the 29 days of BVOC measurements, called “events” in the initial version of manuscript. Otherwise, the appellation of “event” does not refer to NPF event day. Thanks to referee #2 comment, the authors realized that the use of the term “event” in this section can lead to confusion. As a result, the 5 specific periods are now called “episodes” in the revised manuscript.

The suggestion of referee #2 in making mean diel cycle Figures, summarizing the different NPF event day classes observed is relevant. The authors hope that Figure 10 of the revised manuscript (see authors’ response 9) showing mean diel variations for some meteorological parameters (solar radiation, relative humidity and temperature) and BVOCs (isoprene and monoterpenes) among others meets referee #2’s expectations on this point.

As suggested by referee #2, the orange color used to represent solar radiation data has been darkened.

Figure 5 of the revised manuscript is the following:


episode 1
episode 2
episode 3
episode 4
episode 5
Boundary Layer height (m)
Wind speed (m.s-1)
Solar radiation (W.m-2)
Temperature (°C)
Prepicipation (mm)
Relative humidity (%)
Isoprene (ppt)
01/03/2015
07/03/2015
13/03/2015
19/03/2015
25/03/2015
31/03/2015

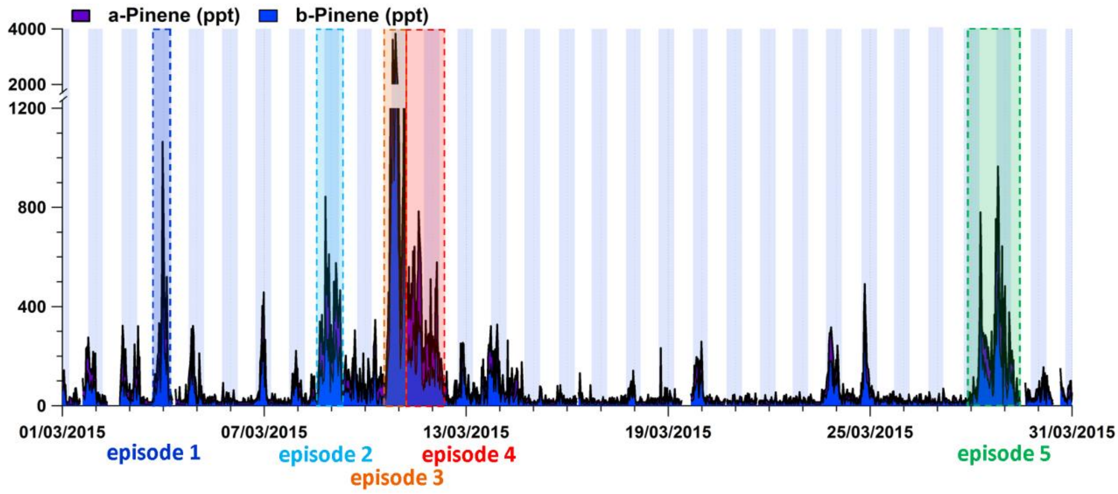


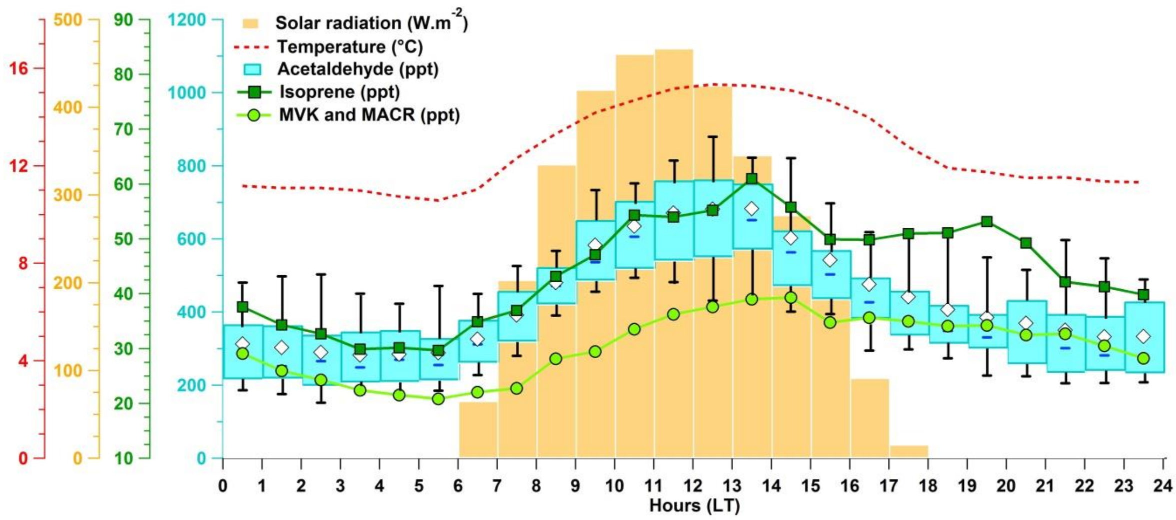
Figure 5: Time series of isoprene and a selection of monoterpenes (α-pinene and β-pinene) in comparison with time series of meteorological parameters (boundary layer height, wind speed, solar radiation, temperature, precipitation and relative humidity). Blue rectangles correspond to nighttime periods. BVOC episodes 1 to 5 referred to specific BVOC variations discussed in Sect. 3.2. Note that, PBL assimilated data were generated by the ECMWF Era-Interim global atmospheric reanalysis at the location corresponding to the Troodos station (32.88° E – 34.92° N, ~20 km westerly from the CAO station).

8/ Figure 7 again, please avoid yellow. I do not really understand the difference between the first and the second panel, other than the second panel shows the same information as Panel 1, with added Methanol diel cycle. Maybe those two can be summarized in one panel? If there is a good reason to keep the first two panels separated, please explain it somewhere. I am not sure, which days are summarized here? Does that Figures include all measurement days? NPF event days, non-event days?

The first panel of Figure 7 highlights the delay of about 1 hour in the peak values between isoprene and its first oxidation products (MVK+MACR). On the second panel, BVOC concentrations are scaled differently than on the first one, which may make less obvious the occurrence of this delay. Considering the recommendation of referee #2, the panel 1 was moved to the Supplement (as Figure SI-3), in order to make Figure 7 of the revised manuscript less extensive.

Figure 7 includes all measurement days with a PTR-MS, i.e. from 1 March to 29 March 2015, which has been explicit in its caption. This period includes NPF event days and non-event days since the variation of acetaldehyde and methanol concentrations was studied independently from this element.

Figure 7 of the revised manuscript is the following:



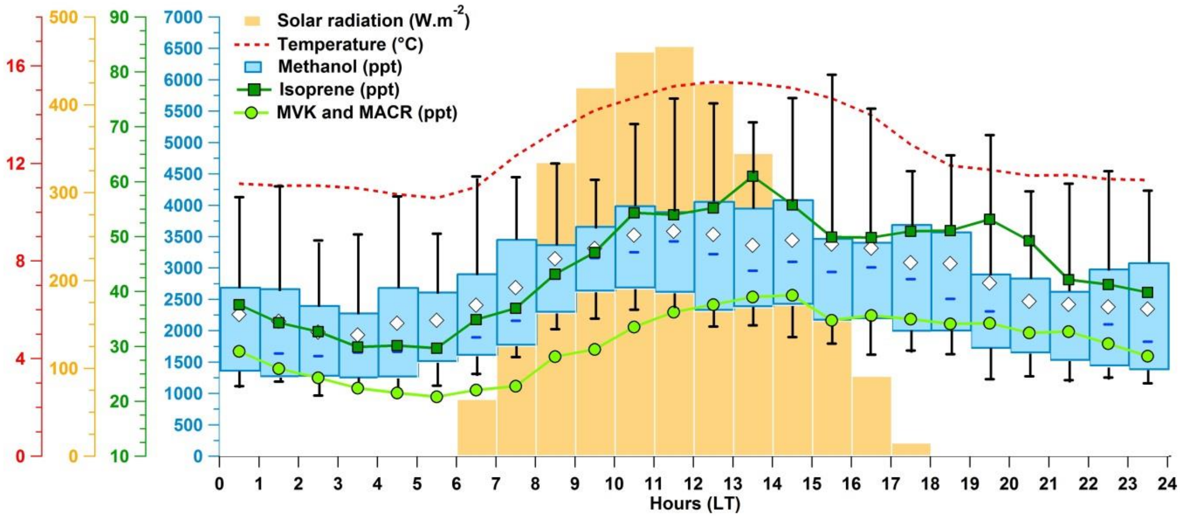


Figure 7: Diel variation of methanol and acetaldehyde, represented by hourly box plots (in blue colors) in comparison with mean diel variation of meteorological parameters (solar radiation, temperature displayed as red lines and orange boxes, respectively) and isoprene and its oxidation products (in green colors). This figure includes all measurement days with a PTR-MS (i.e. from 1 to 29 March 2015). White marker represents the mean value, blue solid line represents the median value and the green 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 the first and the ninth deciles (i.e. D1 and D9). Time is given in local time (UTC + 2 h).

Figure SI-3 of the Supplement is the following:

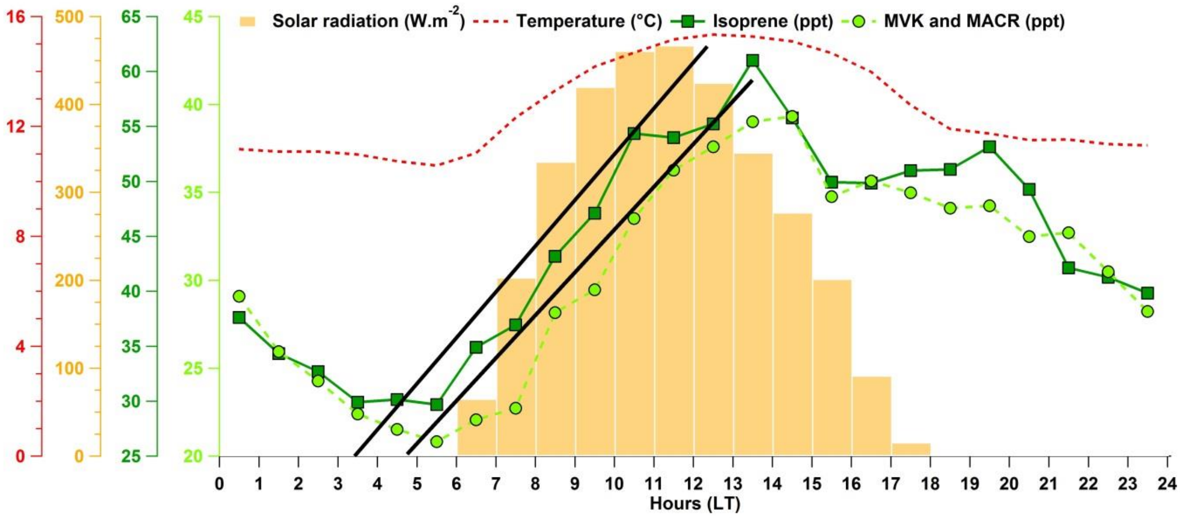


Figure SI-3: Mean diel variation of isoprene and its oxidation products (in green colors) in comparison with mean diel variation of meteorological parameters (solar radiation, temperature displayed as red lines and orange boxes, respectively). This figure includes all measurement days with a PTR-MS (i.e. from 1 to 29 March 2015).

9/ For Figure 9, I have a very similar comment as for Figure 5. It is easier to understand the information if the different NPF event day classes are summarized as mean diel cycle Figure. Again, yellow on yellow.

We understand that it can be difficult to extract the information from Figure 9 (of the initial version of the manuscript), considering the number of parameters explored and the number of measurement days. As suggested by referee #2, mean diel variations of CS and SO_2 concentrations for the different NPF event day classes and for non-event days were added to Figure 11 (of the initial version of the manuscript – Figure 10 of the revised manuscript). Note that, diel variations of the selected parameters during NPF2 event days are now displayed in orange (instead of yellow) in Figure 10 (of the revised manuscript).

As a complement to Figure 10 (of the revised manuscript), Figure 9 (of the revised manuscript) presents mean diel variations of particle numbers (N_{PSM}, $N_{PSM-DMPS}$ and N_{DMPS}) and accumulated diel variations of PM_1 contributions.

Otherwise, Figure 9 (of the initial version of the manuscript) was kept in the revised version of the manuscript, but shifted to the Supplement as Figure SI-4. Considering the number of measurement days for DMPS and PSM (i.e. 20 days), the 4 NPF event day classes are at best represented by 4 event days. So the authors think that Figure SI-4 enables to study suspected parameter influences for each NPF event day individually, nuancing hence the statistical vision of the results given in Figures 9 and 10 (of the revised manuscript). For instance, according to Figure 10 (of the revised manuscript), high concentrations of monoterpenes seem to occur during the nights succeeding NPF2 events (i.e. 8-10 March and 23 March) but, according to Figure SI-4, high concentrations of monoterpenes were mainly observed during the night of the 10th of March. An additional importance of Figure SI-4 is the presentation of air mass origins.

Additionally, H_2SO_4 concentrations are presented in violet (instead of light orange) and NPF2 event days are depicted in orange (instead of yellow) in Figure SI-4.

Figures 9 and 10 of the revised manuscript are the followings:

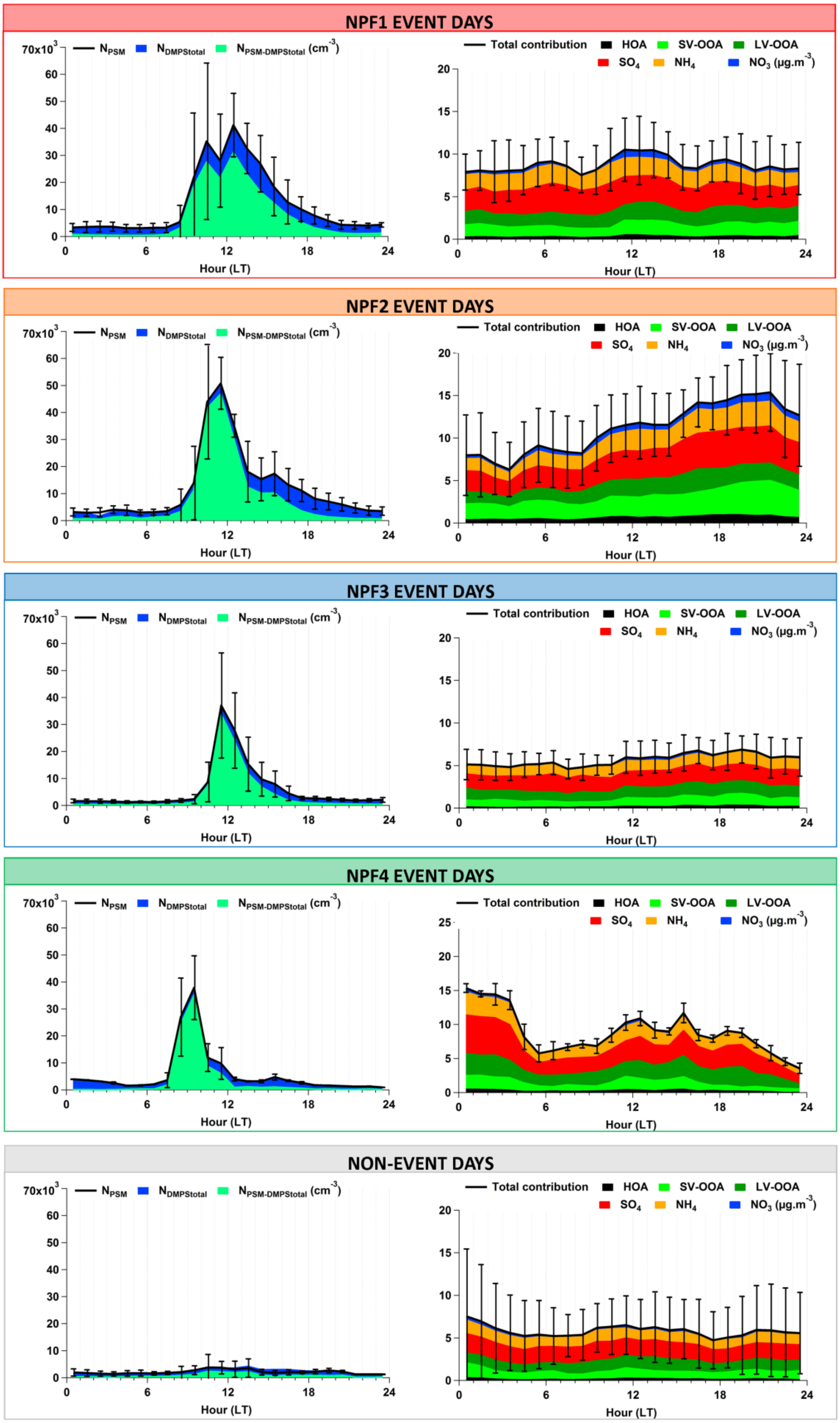


Figure 9: Diel variation of particle number N_{PSM} and N_{DMPS} and accumulated diel variations of PM_1 contributions for NPF event days (NPF1-NPF4) and non-event days. Diel variations are represented by daily mean values associated with standard deviation when several days were combined. Time is given in local time (UTC + 2 h).

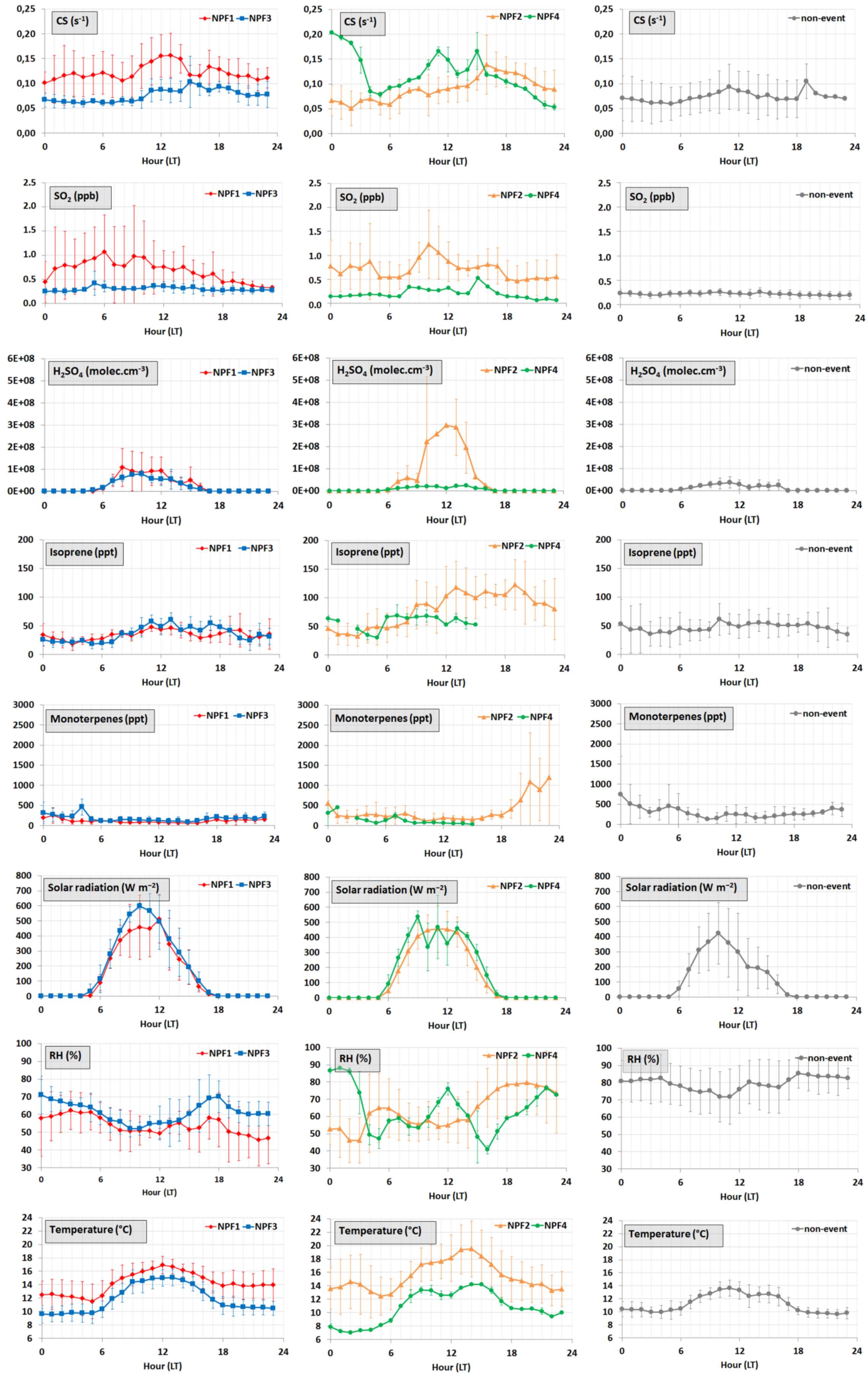

CS (s⁻¹)
NPF1
NPF3
NPF2
NPF4
non-event
SO₂ (ppb)
H₂SO₄ (molec.cm⁻³)
Isoprene (ppt)
Monoterpenes (ppt)
Solar radiation (W m⁻²)
RH (%)
Temperature (°C)
Hour (LT)

Figure 10: Diel variation of CS, SO_2, H_2SO_4, BVOCs (isoprene and monoterpenes) and meteorological parameters (global solar radiation, relative humidity and temperature) during NPF event days (NPF1-NPF4 displayed as red, orange, blue and green lines, respectively) and non-event days (grey lines). Diel variations are represented by daily mean values associated with standard deviation when several days were combined. Time is given in local time (UTC + 2 h).

Figure SI-4 in the Supplement is the following:

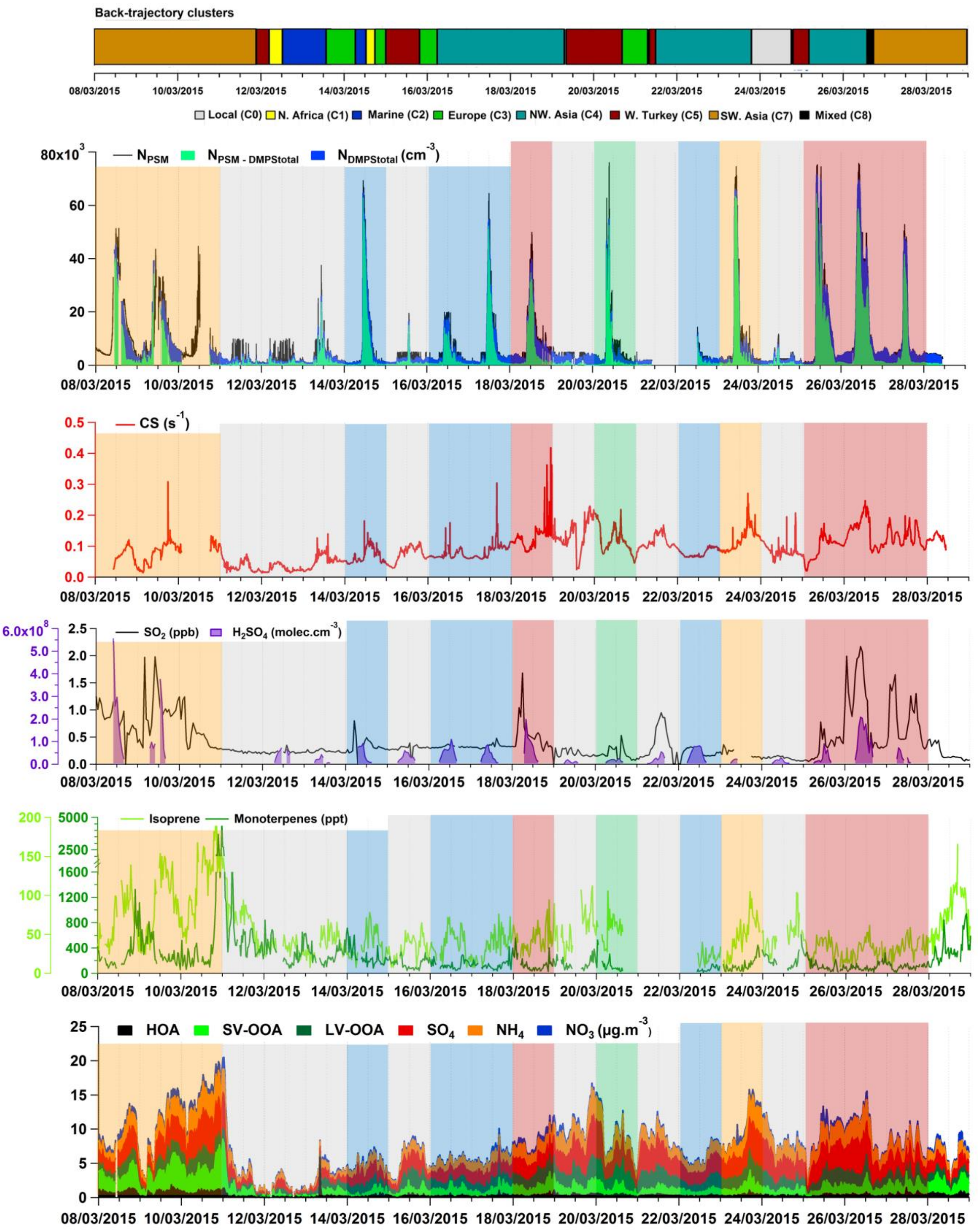


Figure SI-4: Time series of particle number N_{PSM}, N_{DMPS} and CS in comparison with suspected parameters controlling NPF events (SO_2, H_2SO_4, isoprene and monoterpenes) and accumulated time series of PM_1 contribution. The color code highlights NPF event days and non-event days (grey periods). Red periods represent NPF1 event days with

anthropogenic origin. Orange periods represent NPF2 event days both with mixed origins (anthropogenic and biogenic). Blue and green periods are respectively for NPF events of marine (NPF3) and biogenic origin (NPF4). Organic aerosol (OA) factors: HOA - hydrogen-like OA; SV-OOA – semi-volatile oxygen-like OA; LV-OOA – low-volatile oxygen-like OA. Time is given in local time (UTC + 2 h).

10/ I guess you chose the NPF2 in Figure 12, because of the high isoprene concentrations during that event class. I suggest again instead of showing time series of each day separately, to show mean diel cycle plots for the presented parameters comparing NPF2 event days and non-event days before or after NPF2 event days. Again, please avoid yellow on yellow.

The authors chose to further investigate 3 NPF2 event days (8-10 March – NPF event days of mixed origins) since H_2SO_4 and isoprene concentrations were particularly high during NPF2 event days (table 2 of the revised manuscript – authors' response 3) compared to others NPF event days. Similar diurnal variations were also observed between isoprene, temperature and $N_{DMPS-PSM}$ during NPF2 event days (Fig. 9 and 10 of the revised manuscript – authors' response 9) suggesting that isoprene and H_2SO_4 can both play a role during NPF2 event days.

Moreover, higher strength was noticed for NPF2 event day under mixed influence (anthropogenic and biogenic – 23 March) than the ones observed both during NPF1 and NPF4 event days under anthropogenic and biogenic origins respectively, for the same levels of precursors (anthropogenic and biogenic, respectively) suggesting that the combination of biogenic and anthropogenic species forms new compounds which may be involved in nucleation.

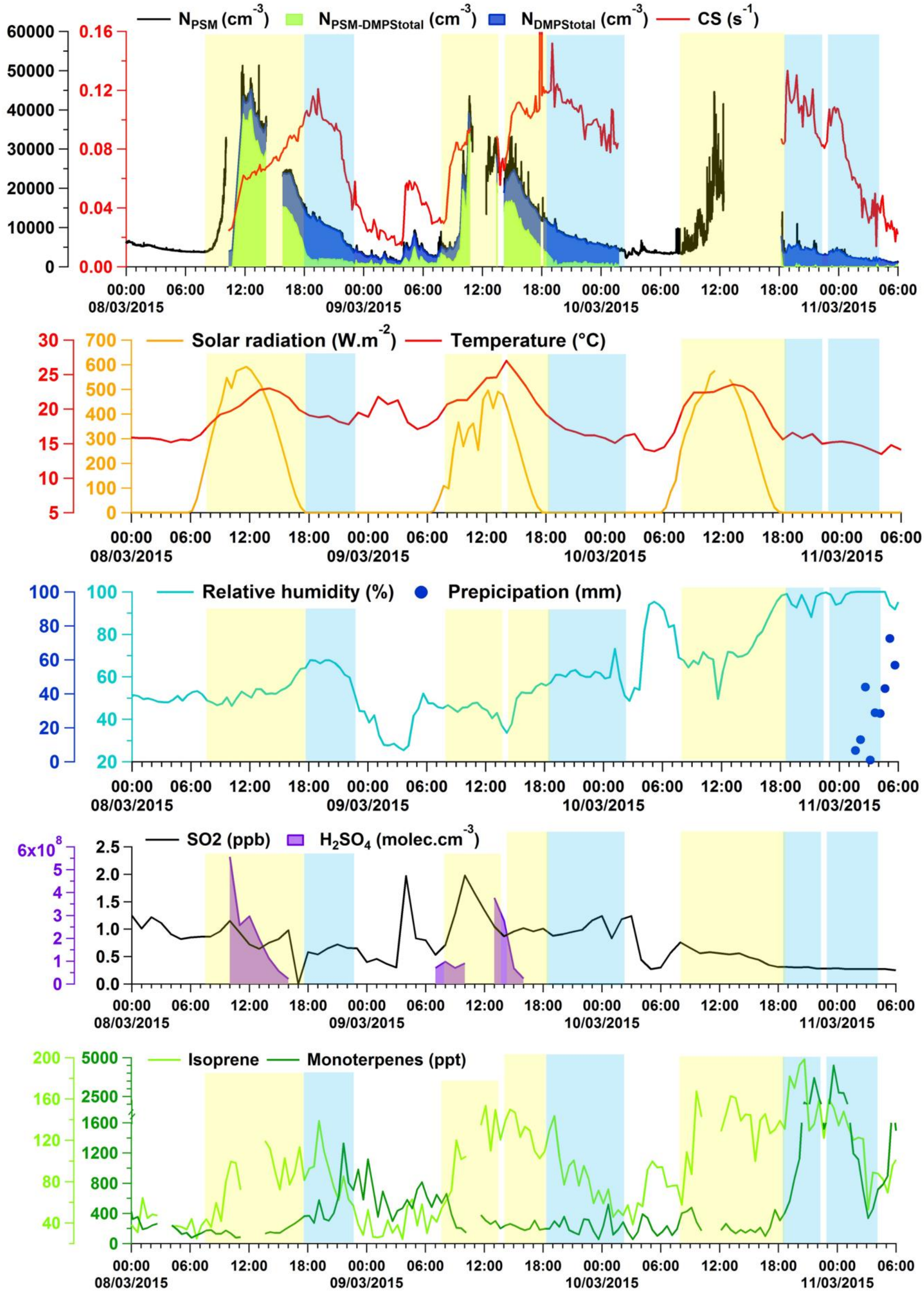
At similar levels of biogenic tracer, NPF2 event on 23 March was characterized by higher particulate formation and growth rates (J_3: 8.97 $cm^{-3}s^{-1}$ - $GR_{1.5-3}$: 3.18 $nm.h^{-1}$) compared to the mean rates characterizing the NPF4 event day of biogenic origin (J_3: 8.13 $cm^{-3}s^{-1}$ - $GR_{1.5-3}$: 1.93 $nm.h^{-1}$). This finding suggests polluted air mixed with high concentrations of biogenic tracers induced more intense particulate formation and faster growth. At higher H_2SO_4 and BVOC concentrations, NPF2 event days occurring on 8-10 March have shown higher particulate formation rates than the one of NPF event on 23 March (J_3: 12.23 $cm^{-3}s^{-1}$ in average ± 5.62 $cm^{-3}s^{-1}$ on 8-10 March and J_3: 8.97 $cm^{-3}s^{-1}$ on 20 March). This finding again, would confirm polluted air mixed with high concentrations of anthropogenic tracers can induce more intense particulate formation.

As a result, the Section 3.4.3 of the manuscript ("Focus on BVOC contributions to particle formation and growth") focuses on 8-10 March (mixed NPF event type) to better understand how the interaction of BVOC species with anthropogenic compounds can initiate nucleation and contributes to early growth of nucleated particles. This section is considered as a case study of 3 specific event days. These days had their specificities, that's why the authors do not prefer presenting results by mean diel cycles, that could biaise interpretations of variations of the selected parameters.

NPF2 event days were compared to non-event days in the previous section and in Figures 9-10 and Table 2 of the revised manuscript. To avoid any redundancy, the authors prefer not showing non-event days in Figure 11.

Additionally, H_2SO_4 concentrations are presented in violet (instead of light orange) in Figure 11 (of the revised manuscript) and orange color used for NH_4 and solar radiation has been darkened while yellow blocks have been lightened.

Figure 11 of the revised manuscript is the following:



N_PSM (cm-3)
N_PSM-DMPStotal (cm-3)
N_DMPStotal (cm-3)
CS (s-1)
60000
50000
40000
30000
20000
10000
0
0.16
0.12
0.08
0.04
0.00
Solar radiation (W.m-2)
Temperature (°C)
30
25
20
15
10
5
700
600
500
400
300
200
100
0
Relative humidity (%)
Prepicipation (mm)
SO2 (ppb)
H2SO4 (molec.cm-3)
6x10^8
2.5
2.0
1.5
1.0
0.5
0.0
Isoprene
Monoterpenes (ppt)
200
160
120
80
40
5000
2500
1600
1200
800
400
0
00:00 06:00 12:00 18:00 00:00 06:00 12:00 18:00 00:00 06:00 12:00 18:00 00:00 06:00
08/03/2015
09/03/2015
10/03/2015
11/03/2015

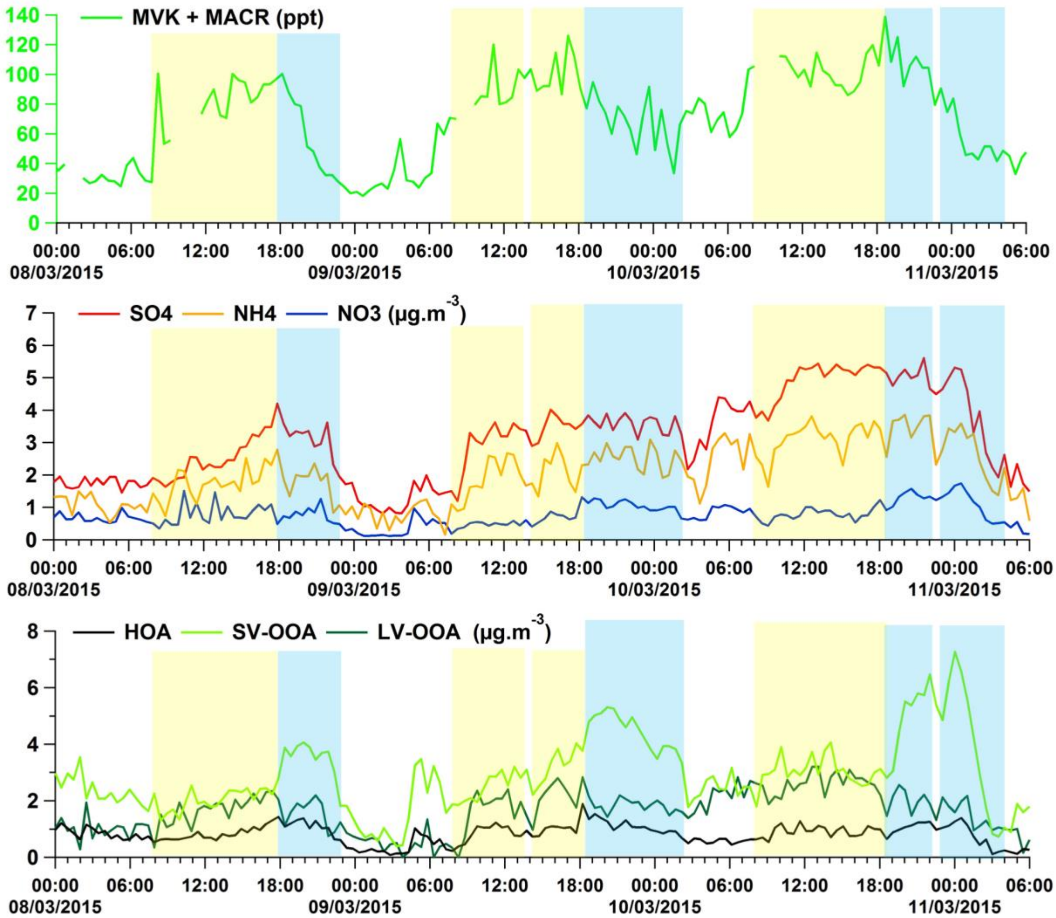


Figure 11: Time series of N_{PSM}, $N_{DMPS,}$ $N_{PSM-DMPS}$ and CS during NPF2 event days (i. e. 08-10 March) in comparison with meteorological parameters (global solar radiation, temperature, relative humidity and precipitation), SO_2, H_2SO_4, BVOCs (isoprene, MVK+MACR and monoterpenes) and PM_1 composition. Time is given in local time (UTC + 2 h). NPF events are represented in yellow and nighttime succeeding these NPF events are depicted in blue. These periods are discussed in Sect. 3.4.3.