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

The manuscript by Debevec et al. describes VOC mixing ratios measured at Cyprus Atmospheric Observatory during one month, March 2015. The motivation for the paper is to find out the driving factors for new particle formation. The measurements cover both on-line and off-line measurements, altogether more than 60 compounds were detected. These kind of intensive campaigns are valuable, since there is still a lot of unknown reactive organic compounds in the atmosphere. Unfortunately, the measurements did not cover sesquiterpenes, since they are likely to be very important in new particle formation and there is very little ambient data of sesquiterpene mixing ratios. The paper is well written, it includes nice, informative figures and it suits well to be published in ACP after minor revisions described below.

Authors' Responses to Referee #1

We would like to thank the Referee #1 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 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 #1 are mentioned in **blue**, while changes made to the revised manuscript are shown in **green**.

The comments on the manuscript are listed as follows:

1/ It is mentioned that ozone was removed in off-line sampling. MnO_2 removes also sesquiterpenes, which is unfortunate, since SQTs are likely to have an important contribution in SOA formation. How about ozone removal in BVOC on-line measurements? How was it removed? In the VOC intercomparison between the used methods on-line measurements showed lower values than off-line measurements. Could this be due to different ozone removal efficiency?

The intensive field campaign was initially carried out at the CAO to provide insights of the origins and fates of VOCs and aerosols in the Eastern Mediterranean, focusing on an extensive high time resolution in-situ measurements performed at a representative receptor site. Instruments deployed during this month make possible the measurement of many tracer compounds from various sources that have been observed at similar rural or remote sites (e.g. Lanz et al., 2008; Leuchner et al., 2015; Michoud et al., 2017; Sauvage et al., 2009; Vlasenko et al., 2009). Considering it was the first intensive field campaign realized at CAO, the authors did not expect to observe such elevated BVOC mixing ratios, especially in March, even if a biogenic potential was noticed considering the site is rather close of oak and pine forests. As a consequence, a specific GC sensitive enough to monitor sesquiterpenes was not deployed in this intensive field campaign. Additionally, sesquiterpenes can be measure with a PTR-MS as they can fragment partly at m/z 205 (Kim et al., 2009). Unfortunately, the authors decided to limit the scan mode of the PTR-MS to m/z 137, in order to have a better time resolution and since no significant levels were noticed at higher m/z (check realized in late February 2015). In a future study, and following the suggestion of referee #1, it could be interesting to investigate sesquiterpene role in NPF formation at CAO.

We didn't use any ozone scrubber for on-line measurements (GCs and PTR-MS). However, as recommended by Detournay et al. (2011), different ozone scrubbers were used during the sampling of off-line measurements presented in section 2.2.1 in order to prevent any ozonolysis of the measured compounds. A KI ozone scrubber was installed upstream of the sampling onto DNPH cartridges, while a MnO_2 ozone scrubber was used for the multi-sorbent cartridges.

In addition to their on-line measurements, α-pinene and acetaldehyde were also measured by off-line techniques. α-Pinene was collected by multi-sorbent cartridges, analyzed after by GC-FID, while acetaldehyde was sampled with DNPH cartridges and analyzed by HPLC-UV. α-Pinene and acetaldehyde were hence chosen to see the potential influence of ozone on on-line measurement by the cross-checking of the results during the field campaign. On-line versus off-line measurements of α-pinene and acetaldehyde concentrations displayed a quite good correlation (r^2: 0.69 and 0.81 for α-pinene and acetaldehyde, respectively) and a slope close to one for both compounds (1.08 and 1.16 for α-pinene and acetaldehyde, respectively). Regarding these results, we think that potential interferences of ozone caused on VOCs measurements with GC systems were limited in this study.

As remarked by referee #1, on-line measurements of the sum of monoterpenes showed lower values than off-line measurements. The authors think that it could be partly due to β-pinene off-line measurements. The authors met some technical difficulties to correctly quantify β-pinene for the off-line method since the calibration results were not reproducible. It could notably affect the concentrations of the sum of monoterpenes for the off-line method, since β-pinene concentrations represented 32 % of the total monoterpene (i.e. the sum of 8 monoterpenes) concentrations.

Additionally, the authors consider that PTR-MS monoterpene measurements were more reliable than off-line monoterpene measurements considering their uncertainties (22 %) that's why on-line measurements were used in this study for the variability investigation of monoterpene concentrations.

2/ It is not quite correct to say that monoterpenes were the most abundant group, when only monoterpenes, isoprene and few oxygenated compounds were measured.

Correction applied in the revised manuscript (Page 11, lines 1 – 2): "Among BVOCs monitored during the intensive field campaign, the most abundant were monoterpenes."

3/ Was isoprene measured with PTR-MS only? As mentioned, also other compounds than isoprene can add to m/z 69, and it would be interesting to see a comparison of isoprene measurement in supplement with other comparisons. High nighttime isoprene concentrations could be due to other compounds fragments too. Inomata et al. conducted such a comparison (ACP; doi:10.5194/acp-10-7085-2010) and found that isoprene measurements with PTR-MS were overestimated in comparison with FID.

During the intensive field campaign, isoprene GC measurements were invalidated since we met technical problems (instability of the baseline around isoprene time response) which did not make possible a correct identification and quantification for isoprene as such levels. This problem was solved after the intensive field campaign, by the replacement of the H_2 generator by compressed H_2 in bottle which permitted to reduced baseline interferences. As a consequence, isoprene was monitored with a GC-FID from late April 2015 to October 2015 and hence comparison of isoprene PTR-MS and GC measurements cannot be done. The authors agree with referee #1 on the fact that nighttime isoprene concentrations could be due to other compounds fragments which was specified in Section 2.2.1 of the revised manuscript.

Correction applied in the revised manuscript (page 6, lines 2-4):
"Note that, nighttime isoprene concentrations discussed in Sect. 3.1 and 3.2 could be due to other compound fragments such as 2-methyl-3-butene-2-ol (MBO)."

4/ It is not self-evident that MBO is temperature and light dependent in a same way as isoprene as mentioned. At least in boreal forest this could not be proved (Tarvainen et al., ACP doi.org/10.5194/acp-5-989-2005).

It was nuanced in the revised version of the manuscript as fallowed (Page 13, lines 4-7):
"~~In contrast to monoterpenes,~~ The emissions of MBO could require light as isoprene (Harley et al., 1998) or could be mainly temperature dependent (Hellén et al., 2018; Tarvainen et al., 2005). Isoprene and/or MBO that were emitted during the late afternoon could be not fully oxidized photochemically, as OH concentrations begin to fall, and could remain in the nighttime atmosphere."

5/ The chapter 3.2 has a misleading title. The manuscript deals with ambient mixing ratios, not with emissions. When discussing variability of the mixing ratios, the atmospheric mixing is not taken into consideration. There is a lot of discussion about the effect of humidity and rain in the mixing ratios, but these can be due to lower mixing layer height. There is currently also another paper under review in ACPD (Hellén et al., doi.org/10.5194/acp-2018-399) which claims that mixing layer height and temperature are the main factors determining ambient mixing ratios. Is there a way to evaluate mixing layer height at CAO if not measured? This would be extremely valuable and needs to be taken into account.

Correction applied in the revised manuscript (page 13, lines 8-13):
"3.2 Factors controlling BVOC concentrations

In this section, time variations of main monoterpenes and isoprene are examined along with meteorological parameters in order to determine the dominant factors controlling BVOC concentrations."

As unfortunately the Planet Boundary Layer (PBL) height was not measured at CAO, we used instead PBL assimilated data conducted for the Troodos station (32.88° E - 34.92° N, ~20 km westerly from the CAO station) which are described in the section S1 added in the Supplement. The comparison of BVOC time series with PBL height was added to the section 3.2 of the revised manuscript and consequently, Figure 5 was modified in the revised manuscript.

Correction applied in the revised manuscript (page 8, lines 19-28):
"2.2.4 Meteorological measurements and assimilated data

Meteorological parameters (temperature, pressure, relative humidity, wind speed, wind direction and radiation) were monitored every 5 min using a weather station (Campbell Scientific Europe, Antony, France) located on the roof top of the CAO building, at approximately 5 m a.g.l. Additionally, Planet Boundary Layer (PBL) assimilated data were generated by the European Centre for Medium-Range Weather Forecast (ECMWF) Interim Re-Analysis (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). ERA-Interim model, set-up and dataset are detailed in Sect. S1 in the Supplement. Even if these PBL data assimilated were not provided for the CAO station but for the Troodos one, they were only used in this study to qualitatively investigate PBL height effect on BVOC concentration levels and variations."

Additional information added in the revised manuscript (from page 13, line 14 to page 14, line 5):

"Firstly, diurnal variability of BVOC concentrations seems to be driven by the vertical mixing. Low pinene concentrations were measured during the day when PBL heights were the highest, that could be due to efficient sink reactions with OH radicals and dilution by vertical transport. The highest pinene concentrations during the night correspond to lowest mixing. The biogenic compounds emitted during the night were probably trapped in a nocturnal inversion layer, and their concentrations build up until they were diluted in the morning by mixing. The effect of PBL height on monoterpene concentrations was observed in other studies, such as ones dedicated to SMEAR II results (measurements conducted to a boreal forest site in southern Finland - Hakola et al., 2012, 2000; Hellén et al., 2018; Sellegri et al., 2005). Contrarily, isoprene concentrations were higher during the day compared to nocturnal ones, suggesting that the diurnal variability of its concentrations is not influenced by the vertical mixing. Beside the daily variability of the PBL, its height range along the month may influence the BVOC concentration levels. Pinene episodes 2-5 occurred following days when daily maxima PBL heights were the lowest observed of the intensive field campaign, suggesting less dilution of the emitted compounds. However, PBL height effect on pinene concentrations was not systematically observed. For instance, higher pinene concentrations (up to 1100 ppt) were observed during event 1 (i. e. 3 March) compared to pinene levels recorded on the days before and after episode 1 while daily maximal PBL heights were of the same range from 1 to 5 March. The day before episode 5 (i.e. 27 March) was characterized by a daily maximal PBL height as low as episode 2-5 ones, even if no significant pinene concentrations were observed. Furthermore, the highest isoprene daily concentrations of the month (i.e. 1-3 and 28 March) were observed during days characterized by low PBL heights. Again, PBL height effect on isoprene concentrations seems to be not systematic.

In addition to vertical mixing, wind transport could also influence BVOC concentrations. Wind speeds are generally higher during daylight hours compared to nighttime values in March 2015, inducing more dispersion of BVOC emissions during the day. The five episodes occurred under calm low wind condition, which could promote the accumulation of BVOCs in the atmosphere. Contrarily, from 21 March to 23 March, wind speeds were up to 12 $m.s^{-1}$ and no significant pinene concentrations were observed during these days. Furthermore, the highest isoprene daily concentrations of the month (i.e. 1-3 and 28 March) were observed during days characterized by quite low wind speeds. However, wind speed effect on BVOC concentrations seems to be not systematic."

Correction applied in the revised manuscript (page 15, lines 12-17):

"As a summary, BVOC concentration levels and variations could be explained by sources, sinks, vertical mixing along with horizontal transport. BVOC emissions have shown to be controlled by ambient temperature, precipitation and relative humidity. More specifically, significant increases in monoterpene mixing ratios occurred during and after rainy periods and the stimulation of pinene emissions by rainfall seemed to be responsible for additional emissions of monoterpenes during the daytime. High relative humidity seemed to promote high BVOC concentrations originating from the nocturnal biogenic source (i. e. oaks and pines forests)."

Section S1 in the Supplement is the following:

"S1 Planet Boundary Layer (PBL) assimilated data

In order to investigate PBL height effect on BVOC concentrations, this parameter was evaluated using PBL assimilated data generated by the European Centre for Medium-Range Weather Forecast (ECMWF) Interim Re-Analysis (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).

The ERA-Interim dataset starts from 1979 and continues to provide information until present in near real-time. Gridded data products include a large variety of 3-hourly surface parameters, describing weather as well as ocean-wave and land-surface conditions, and 6-hourly upper-air parameters covering the troposphere and stratosphere. Vertical integrals of atmospheric fluxes, monthly averages for many of the parameters, and other derived fields have also been produced. Berrishford et al. (2011) provide a detailed description of the ERA-Interim product archive. ERA-Interim products are normally updated once per month, with a delay of two months to allow for quality assurance and for correcting technical problems. The ERA-Interim atmospheric model has a spatial resolution of 0.75°x0.75° and expands vertically with 60 atmospheric layers. The reanalysis product is produced with a sequential data assimilation scheme, using 12-hourly analysis cycles , a time-window when available observations are assimilated into the information from the forecast model as described in Dee et al. (2011).

The ERA-Interim model includes a PBL height parameter calculated from the Bulk Richardson number (Troen and Mahrt, 1986), which is based on ratios of both dynamic and thermodynamic vertical gradients and hence characterizes the degree of turbulence. Given the fact that the boundary layer is often associated with stronger mixing (as compared to the free troposphere) due to increased levels of turbulence, it would be natural to investigate properties associated with turbulence. Essentially, the PBL height is defined as the level where the bulk Richardson number reaches a critical value of 0.25, based on the difference between quantities at this level and the lowest model level as an estimator for the vertical stability. Bulk Richardson number is available a 6-h and 12-h forecasts.

However, as reported in von Engeln and Teixeira (2013) this method of estimating the stability from dry thermodynamic variables (not moist), tends to provide estimates of PBL height that is often closer to the cloud-base height in marine cloudy boundary layers, rather than the PBL height itself (Janssen and Bidlot, 2003). Seidel et al. (2012) reports that for their scope of assessing the climatology of the planetary boundary layer over the continental United States and Europe with the use of ERA-Interim datasets, they did not employ the estimates of the BLH from ERA-Interim itself, because they are computed using an algorithm not applicable to radiosonde data (due to the fact that turbulence parameters are required for this application). With a preliminary analysis, they report that the ERA-interim PBL height product (i.e., with the ECMWF algorithm) shows higher heights, especially over high elevation regions, than the algorithm used in their study on the radiosonde data. Differences were below 100 m at night and of several 100 m during daytime."

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Dee D. P., Uppala S. M., Simmons A. J., Berrisford P., Poli P., Kobayashi S., Andrae U., Balmaseda M. A., Balsamo G., Bauer P., Bechtold P., Beljaars A. C. M., van de Berg L., Bidlot J., Bormann N., Delsol C., Dragani R., Fuentes M., Geer A. J., Haimberger L., Healy S. B., Hersbach H., Hólm E. V., Isaksen L., Kållberg P., Köhler M., Matricardi M., McNally A. P., Monge-Sanz B. M., Morcrette J.-J., Park B.-K., Peubey C., de Rosnay P., Tavolato C., Thépaut J.-N., Vitart F., 2011. The ERA-Interim reanalysis: configuration and performance of the data assimilation system. Q. J. R. Meteorol. Soc. 137, 553–597. https://doi.org/10.1002/qj.828

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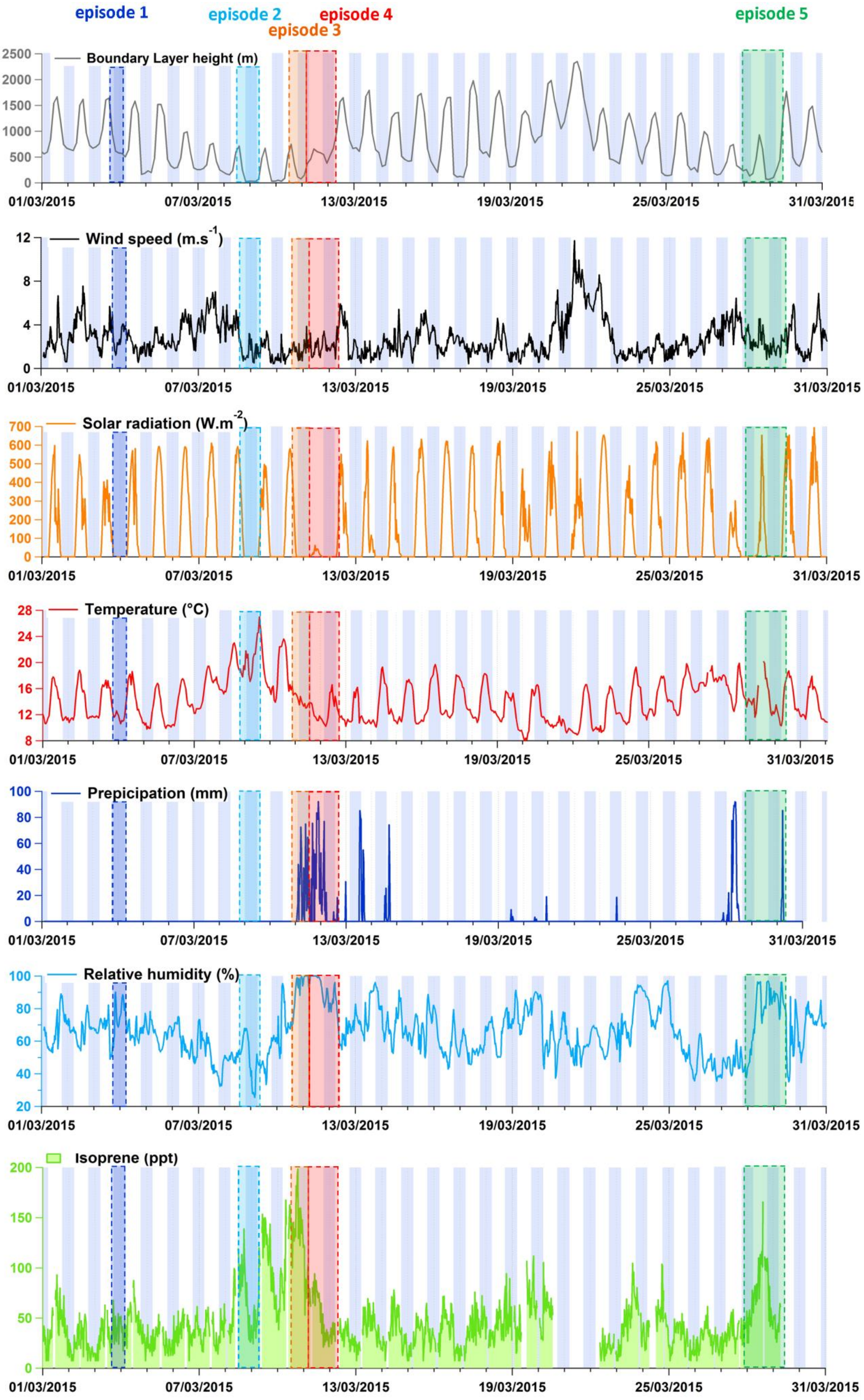
Revised Figure 5 is the following:


episode 1
episode 2
episode 3
episode 4
episode 5
Boundary Layer height (m)
2500
2000
1500
1000
500
0
01/03/2015
07/03/2015
13/03/2015
19/03/2015
25/03/2015
31/03/2015
Wind speed (m.s^{-1})
12
8
4
0
Solar radiation (W.m^{-2})
700
600
500
400
300
200
100
0
Temperature (°C)
28
24
20
16
12
8
Prepicipation (mm)
100
80
60
40
20
0
Relative humidity (%)
100
80
60
40
20
Isoprene (ppt)
200
150
100
50
0

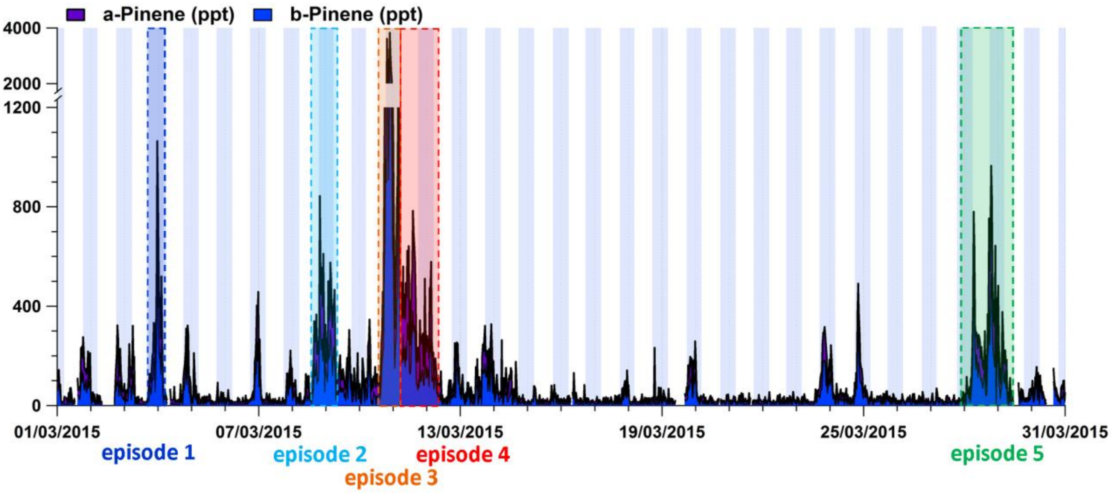


Figure 5: Time series of isoprene and a selection of monoterpenes (α-pinene and β-pinene) in comparison with time series of meteorological parameters (boundary layer height, wind speed, solar radiation, temperature, precipitation and relative humidity). Blue rectangles correspond to nighttime periods. 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).

6/ Acetaldehyde is a known product of myriad of atmospheric reactions, for example OH radical reactions. OH radicals are produced only in sunlight and therefore acetaldehyde mixing ratios would also peak during daytime. The following sentence is from Millet et al. (ACP, 2010) abstract: "Hydrocarbon oxidation provides the largest acetaldehyde source in the model (128 Tg a-1, a factor of 4 greater than the previous estimate), with alkanes, alkenes, and ethanol the main precursors. There is also a minor source from isoprene oxidation". Why are the authors convinced that VOC oxidation is not the cause for high midday acetaldehyde mixing ratios, but light dependent emissions?

From the 6 PMF factors reported in Debevec et al. (2017), the measured OVOCs were distributed among their different sources (Fig. 6). More than 80 % of the respective total mass of methanol, acetaldehyde and MVK+MACR was explained by biogenic sources, namely by factor 2 driven by isoprene emissions. The morning increase pattern of acetaldehyde concentration is similar to isoprene pattern rather than isoprene oxidation product one that could suggest that acetaldehyde was mostly released in the atmosphere by local vegetation rather than produced by VOC oxidation processes in March 2015.

Correction applied in the revised manuscript (Page 16, lines 15-24):
"Hydrocarbon oxidation (mostly alkanes and alkenes but also isoprene and ethanol) provides the largest acetaldehyde source in the budget estimates of Millet et al. (2010). Nonetheless, for all reaction pathways of isoprene with atmospheric oxidants, acetaldehyde is produced as a second- or higher-generation oxidation product of isoprene (Millet et al., 2010). In addition to photochemical production, acetaldehyde is emitted by terrestrial plants, as a result of fermentation reactions leading to ethanol production in leaves and roots (Jardine et al., 2008; Rottenberger et al., 2008; Winters et al., 2009). ~~Along with methanol and isoprene, acetaldehyde showed a similar trend with a clear diurnal cycle with a daytime maximum consistent with temperature.~~ Acetaldehyde concentrations started to increase in the morning and peaked at midday followed by a gradual decrease throughout the rest of the day. The morning increase

pattern of acetaldehyde concentrations is similar to the isoprene pattern rather than isoprene oxidation product one and isoprene and acetaldehyde ~~also~~ correlated well (r^2 = 0.49). These findings suggest~~ing~~ that acetaldehyde was mostly released in the atmosphere by local vegetation rather than produced by VOC oxidation processes in March 2015.

7/ Table showing the mean mixing ratios of individual compounds would be helpful

The table showing statistics of mixing ratios of individual compounds was added to the Supplement of the revised manuscript as Table SI-1.

Table SI-1 in the Supplement is the following:

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.**
DIENE	**Isoprene**	4	26	38	46	53	219	28	21	11
TERPENES	**α-Pinene**	8	8	18	58	58	1874	131	16	10
	β-Pinene	6	6	18	61	57	1962	142	12	12
	Camphene	<1	5	11	25	29	275	37	1	ND
	Myrcene	<1	2	4	6	8	43	7	2	ND
	Δ^3-Carene	<1	4	8	11	15	91	11	1	ND
	α-Terpinene	<1	1	2	3	5	32	4	1	ND
	γ-Terpinene	<1	<1	<1	<1	1	12	2	1	ND
	Limonene	<1	8	17	27	32	347	37	1	ND
ALCOHOL	**Methanol**	654	1658	2426	2765	3452	9074	1452	180	21
CARBONYL COMPOUNDS	**Formaldehyde**	399	678	909	986	1170	2416	409	25	ND
	Acetaldehyde	102	277	390	431	531	1533	209	44	10
	Acetone	423	861	1048	1083	1214	2662	335	17	9
	MVK+MACR	3	19	26	30	35	139	18	3	12
	MEK	59	154	196	210	242	653	84	13	9

ND: not determined