We thank anonymous referee (2) for revising the manuscript and providing helpful comments and suggestions.

Anonymous referee (2)

General comments:

Zanoni et al. report the first total OH reactivity dataset from a Mediterranean receptor site acquired during the summer of 2013 within the framework of the CHARMEX campaign. The dataset includes comprehensive speciated VOC measurements, along with the total OH reactivity measurements. The measured total OH reactivity at the site was between 3 to 17 s-1, with an average of 5 s-1, co-varying with the air temperature. High missing OH reactivity greater than 50% was observed occasionally which the authors speculate to be majorly due to oxygenated molecules, mostly formed from reactions biogenic trace gases. The results demonstrate that local biogenic emissions are more important than transported pollution at the receptor site for ambient OH reactivity datasets in the literature, especially from remote sites. The paper is well structured and generally well written. I recommend publication in ACP after the following specific concerns/points have been addressed by the authors.

Major points that should be clarified/added in revised MS:

1) (i) The classification of anthropogenic VOCs needs to be qualified. There are several published reports now that show release of aromatic compounds from stressed vegetation (e.g. Misztal, P. K. et al., Scientific Reports (Nature Publishing Group), 5, 2015. Have the authors examined the co-variation of aromatics with ambient temperature?

(ii) We thank the referee for this comment and idea. The proposed classification can be a bit controversial since many of the measured compounds can be emitted by more sources, as mentioned by the referee for the aromatic compounds. At the site, the aromatic compounds had a VMR below 1 ppbv (e.g. benzene maximum VMR was 0.07 ppbv and toluene maximum VMR was 0.14 ppbv, see left axes of the following figure). It is hard to see a trend for benzene, for its concentration is close to the instrumental detection limit. Toluene highest VMR occurred when the air masses were transported from East (North of Italy) and during nighttime when the air temperature was lower (see figure reported below). Therefore it seems unlikely that these compounds have been released due to stressed vegetation at the site and we decided to keep the classification as initially proposed.



2) (i) Use of PMF factors and data: Too many in prep papers (e.g. Michoud et al.) are being relied upon for interpretation of the results of this MS and since the details of those are unavailable this does weaken the MS a bit. I don't really think it is good idea to show such PMF data in a Figure wherein the primary MS has not yet been published. Few lines attributing it to as personal communication should be enough. The major results of the current paper do not rest on the PMF analyses, so this should be ok. In case you do retain Figure 8, the units of PMF factors should be explained.

(ii) The referee is right. This is also a comment from referee 1. However, we decided to keep the information obtained from PMF analysis because it brings an additional insight into our study. It is important to note that the paper from Michoud et al. is now available (<u>http://www.atmos-chem-phys-discuss.net/acp-2016-955/</u>) and it gives detailed information about the PMF results. Nevertheless, the section has been modified to make the interpretation clearer and less speculative, including explanations of the PMF factors and unit (ppbv) reported in Fig. 8.

(iii) Line 2, page 9, please add:

The data set is considered as a X matrix composed of i samples and j measured chemical species; the analysis decomposes X into a product of two matrices: f the species profiles for each source, g the contribution of the factors to each sample for the minimized residual error e (eq.3). Finally the p factors that drive the concentration of the measured species are determined.

$$X_{ij} = \sum_{k=1}^{p} g_{ik} * f_{kj} + e_{ij}$$
(3)

The optimal solution is found performing the PMF for a number of different factors from 3 to 12. The best solution in terms of residual error, rotational ambiguity and minimum correlation among factor contribution was finally retained in order to have 6 independent factors. From the 6 factors (3 for primary anthropogenic sources, 2 for biogenic sources, 1 for oxygenated molecules from mixed sources both primary as secondary emitted), three are used to help interpreting the OH reactivity data set.

The complete description of PMF analysis performed on the VOC database of the CARBOSOR-ChArMEx campaign is available in Michoud et al., (2017). Figure 8:



Figure 8. Time series of missing OH reactivity (left axis) reported with the factors obtained from positive matrix factorization analysis (right axis): primary-emitted biogenic volatile organic compounds factor (pBVOCs), oxygenated volatile organic compounds factor and secondary biogenic volatile organic compounds factor (sBVOCs). Missing data points of missing OH reactivity correspond to either data points ≤ 0 either data points of missing measured OH reactivity values.

Please substitute section 4.4 and conclusions with:

Insights into the missing OH reactivity

We here consider the contribution of each chemical group to the OH reactivity during the period of the campaign when a significant missing reactivity was observed (23/07/2013 - 30/07/2013).

We first focus on the primary-emitted BVOCs measured: isoprene and monoterpenes. Isoprene was measured by both PTR-MS and GC and the results correlated within the measurement uncertainty (slope and R^2 of the regression for 415 data points are 0.93 ± 0.03 and 0.77, respectively; see supplement). A small offset in the scatter plot (approximately 100 ppt) may indicate a small interference at m/z 69 for the PTR-MS measurements.

Individual monoterpenes were either sampled on-line through GC-FID, or collected on adsorbent tubes to be analysed in the laboratory through GC-MS shortly after the campaign. At the same time, monoterpenes were also measured by PTR-MS as total monoterpene fraction since the instrument cannot distinguish between structural isomers. We compared the total monoterpene concentration observed by PTR-MS to the summed monoterpenes concentration from GC techniques and calculated a concentration difference between 0.2 and 0.6 ppbv(see supplement). Although small, the difference observed is significant, being outside the combined measurement uncertainty. Here, the summed calculated OH reactivity is obtained from data of isoprene and monoterpenes measured

by GC. The unmeasured compounds could be either monoterpenes not detected individually, or monoterpenes lost in the sampling tubes after being collected. We roughly estimated how much OH reactivity can result from unmeasured monoterpenes: a number of monoterpenes emitted by Mediterranean plants surrounding the monitoring station were considered and a weighted reaction rate coefficient with OH of 1.56×10^{-10} cm³ molecule⁻¹ s⁻¹ was determined from them (see rosemary from Bracho-Nunez et al., 2011). A volume mixing ratio of 0.2-0.6 ppbv of missing monoterpenes results in 0.8-2.3 s⁻¹ of OH reactivity, which, even in the upper limit, is too low to explain the missing OH reactivity for the specific time frame, including during nighttime.

Figure 6 shows the volume mixing ratios of BVOCs and oxidation products variability with local drivers, such as temperature, wind speed and solar irradiance. Volume mixing ratios are reported for the protonated masses measured by PTR-MS, including: m/z 69 (isoprene) and m/z 137 (monoterpenes) for the primary-emitted BVOCs, and m/z 71 (isoprene first generation oxidation products: Methyl Vinyl Ketone (MVK) + methacrolein (MACR) + possibly isoprene hydroxyperoxides (ISOPOOH)), m/z 139 (nopinone, β -pinene first generation oxidation product), m/z 151 (pinonaldehyde, α -pinene first generation oxidation product) and m/z 111, m/z 113 oxidation products of several terpenes. As recently reported by Rivera-Rios et al., 2014, the m/z 71 might also include the ISOPOOH which could have formed at the site and fragmented inside the PTR-MS. However, it is important for the reader to know that we did not separate the different components of the m/z 71, therefore the presence of ISOPOOH on m/z 71 is assumed based on the recent literature. For all the above mentioned masses, except for m/z 111 and m/z 113, the corresponding rate coefficient of reaction with OH of the unprotonated molecule was found and their OH reactivity summed in the calculated OH reactivity. The reported time series show that both primary BVOCs and most of the OVOCs resulting from their oxidation had a diurnal profile. Temperature, light and wind speed affected both isoprene and m/z 71 while monoterpenes and corresponding products were more influenced by temperature and wind speed. Contrastingly, m/z113 was also present during nighttime in low amounts, which might indicate the presence of more oxidation products associated with its formation present during the night. A sharp increase of m/z71, m/z 113, m/z 139 began after 26/07 when wind speed was lower and increased again after 27/07 when also air temperature was higher. Although only a fair correlation was found for the measured OH reactivity with some masses, generally higher coefficients for all masses and good correlation coefficients of the linear regressions, specifically for m/z 71, m/z 111 and m/z 151 were found from July 27th to 30th. Some of these oxidation products (m/z 111, m/z 113, m/z 151) have already been observed in chamber and field studies (Lee et al., 2006, Holzinger et al., 2005) as they are formed from the photo-oxidation of different parent compounds belonging to the class of terpenes. Interestingly, the highest yields of the mentioned products were attributed to terpenes also common to the Mediterranean ecosystem, such as myrcene, terpinolene, linalool, methyl-chavicol and 3carene (Lee et al., 2006, Bracho-Nunez et al., 2011).

The effect of temperature was also considered for the period of missing OH reactivity. However, it was only from July 27th that the missing reactivity showed a clear temperature dependence. Terpenes emissions are temperature dependent. Their emissions are usually fitted to temperature with the expression $E(T) = E(Ts)\exp[\beta(T - Ts)]$, where E(Ts) is the emission rate at Ts, β the temperature sensitivity factor and T is the ambient temperature. The dependence of the missing reactivity on temperature was originally demonstrated by Di Carlo and coworkers for a temperate

forest in northern Michigan (Di Carlo et al., 2004). They found the same temperature sensitivity factor for the missing reactivity as for terpenes, β = 0.11 K⁻¹, with a correlation coefficient of R²=0.92. Following the same approach, Mao et al., (2012) reported a β factor of 0.168 K⁻¹ from a study in a temperate forest in California. They were able to explain the discrepancy between the measured reactivity and the calculated reactivity simulating the species formed from the oxidation of the BVOCs. Figure 7 displays a scatter plot of the missing OH reactivity observed during this study as a function of ambient temperature. Here, the coefficients β = 0.173 K⁻¹ and R²=0.568 were found when data from July 27th -30th are plotted, whereas a weaker correlation and higher coefficient is found for data within the July 23rd -26th period. From the similarities with the study of Mao et al., (2012) we think that unmeasured oxidation products of BVOCs could be the dominant cause of missing OH reactivity at our field site. However, it should be noted that the missing OH reactivity can be influenced by processes that do not affect BVOC emissions, such as boundary layer height and vertical mixing (see also comments reported in Hansen et al., 2014).

Positive Matrix Factorization analysis on the collected VOCs data sets at the site identified 6 independent factors. These describe the source of the VOCs which includes: a primary biogenic factor (pBVOCs), a secondary biogenic factor (sBVOCs) and an oxygenated factor. The factor represtenting pBVOCs is composed of short-lived molecules directly emitted by biogenic sources, such as isoprene and the sum of monoterpenes. sBVOCs factor is composed by secondary oxidation products of biogenic-emitted molecules, such as: MVK+MACR, nopinone and pinonaldehyde. The oxygenated factor includes oxygenated molecules of mixed origin, both primary and secondary emitted, such as carboxylic acids, alcohols and carbonyls. Figure 8 reports the variability of the three factors: during daytime this is predominantly by pBVOCs and sBVOCs, while during nighttime it is driven by oxygenated molecules. Additionally, pBVOCs factor significant contributes to the OH reactivity during the whole campaign period, while sBVOCs factor is more variable, higher during the missing OH reactivity event, suggesting a significant impact of unmeasured secondary species to the missing OH reactivity.

Conclusions

The total OH reactivity was used in this study to evaluate the completeness of the measurements of reactive trace gases at a coastal receptor site in the western Mediterranean basin during three weeks in summer 2013 (16/07/2013-05/08/2013). OH reactivity had a clear diurnal profile and varied with air temperature, suggesting that biogenic compounds were significantly affecting the local atmospheric chemistry. Ancillary gas measurements confirmed that most of the reactivity during daytime was due to biogenic VOCs, including relevant contributions from oxygenated VOCs, while during nighttime inorganic species and oxygenated VOCs had the largest contribution. The OH reactivity was on average 5 ± 4 s⁻¹ (1 σ) with a maximum value of 17 ± 6 s⁻¹ (35% uncertainty). The observed maximum is comparable to values of OH reactivity measured at forested locations in northern latitudes (temperate and boreal forests as reported by Di Carlo et al., 2004, Ren et al., 2016, Sinha et al., 2010, Noelscher et al., 2013, Kumar and Sinha, 2014 and Nakashima et al., 2014). This finding highlights the importance of primary-emitted biogenic molecules on the OH reactivity, especially where air temperature and solar radiation are high; even though our site was

specifically selected for a focused study on mixed and aged continental air masses reaching the basin.

A comparison between the measured OH reactivity and the summed reactivity from the measured species showed that on average 56% of the measured OH reactivity was not explained by simultaneous gas measurements during 23/07/2013-30/07/2013. During this period, the air masses originated from the West (23/07/2013-27/07/2013 and 29/07/2013-30/07/2013) and the South (27/07/2013-29/07/2013); calm wind conditions and peaks of air temperature were registered at the field site (28/07/2013). In contrast, when the site was exposed to air masses from the eastern and northern sectors, namely northern Italy and South of France, weak pollution events mostly enriched by anthropogenic gases were observed. In such cases, the measured and calculated OH reactivity values were in agreement. During 23/07/2013-30/07/2013 we observed increased concentration of BVOCs and OVOCs, lack of pollution events, higher temperature and relatively high missing reactivity (~10 s⁻¹). Specifically, a maximum value of 2.3 s⁻¹ of OH reactivity was estimated for unmeasured primary BVOCs, namely non-oxygenated monoterpenes. Such missing reactivity is not linked to any specific event and is rather distributed along the whole time frame of the campaign.

During 27/07/2013-30/07/2013 an increase in oxygenated VOCs originating from the photooxidation of primary-emitted BVOCs was also detected. Highest yields of these oxidation products $(m/z \ 111, m/z \ 113, m/z \ 151)$ were attributed to terpenes, which are emitted in abundance by Mediterranean ecosystems (Lee et al., 2006, Bracho-Nunez et al., 2011). We found that the missing reactivity during 27/07/2013-30/07/2013 had a similar temperature dependency to a reported study conducted in a temperate forest in the US, for which model predictions highlighted that unmeasured oxidation products of BVOCs could explain the missing reactivity (Mao et al., 2012). We conclude that, specific to this period and ecosystem, unmeasured oxidation products of terpenes could be the cause of the observed discrepancy between measured and calculated OH reactivity. Complementary analysis, including PMF, helped confirm the influence of the secondary biogenic VOCs and highlighted the influence of oxygenated molecules during nighttime and part of the missing reactivity period (July 23^{rd} - 27^{th}).

Mediterranean plants are known to emit large quantities of reactive BVOCs, including sesquiterpenes and oxygenated terpenes (Owen et al., 2001), which were not investigated during our fieldwork. We assume therefore that these molecules, as well as their oxidation products, might also have played an important role in the missing OH reactivity detected.

We can therefore answer the research questions addressed in the introduction, as the presence of missing reactivity reveals that some reactive compounds were not measured during the fieldwork. Most of these molecules were likely oxidation products of biogenic compounds. Two main conclusions are obtained from this study: first, although several state-of-the-art instruments were deployed for this campaign, major difficulties are still encountered for the accurate detection of oxygenated chemicals. Second, as various other studies on OH reactivity have pointed out so far, many unknowns are still associated with the photo-oxidation processes of BVOCs.

Further studies with chemical and transport models to identify the important chemical functions of these oxygenated molecules, as well as the effects of long-range transport would be beneficial to provide a complete picture of this work.

Finally, as the Mediterranean basin differs from side to side, (air masses reception as well as type of ecosystems) more intensive studies at different key spots, e.g. western vs eastern basin and remote vs. periurban ecosystems, would be helpful for a better understanding of the atmospheric processes linked to the reactive gases over the Mediterranean basin.



3) (i) The current MS can benefit by including and discussing comparisons with the following relevant studies on OH reactivity measurements from high isoprene concentration sites :

i) Nakashima, Y., Kato, S., Greenberg, J., Harley, P., Karl, T., Turnipseed, A., Apel, E., Guenther, A., Smith, J., and Kajii, Y.: Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign, Atmos. Environ., 85, 1–8, doi:10.1016/j.atmosenv.2013.11.042, 2014.

ii) Kumar V. and Sinha V.: VOC–OHM: A new technique for rapid measurements of ambient total OH reactivity and volatile organic compounds using a single proton transfer reaction mass spectrometer, Int. J. Mass Spectrom., 374, 55–63, doi:10.1016/j.ijms.2014.10.012, 2014.

(ii) We thank the referee for the suggestion, the two studies are included in the conclusion of the manuscript.

Technical comments:

1) (i) Please mention the temperature and pressure values and list the the rate constants used for determining calculated OH reactivity and CRM OH reactivity (the latter can be added to the supplement).

(ii) We thank both referees for this comment. Table 1 is extended with the rate constants of each species considered at ambient temperature (298 K) and atmospheric pressure (please see Table 2 in the supplementary material).

(iii) Table 2 in supplementary material:

Table 2. Rate constants for the reactions with OH of the measured OH reactants.

Molecule	k _{i+OH} (cm ³ molecules ⁻¹ s ⁻¹)	Reference
a-terpinene	3.60E-10	Atkinson, 1986
g-terpinene	1.76E-10	Atkinson, 1986
limonene	1.69E-10	Atkinson, 1986
isoprene	1.00E-10	Atkinson, 1986
2-methyl-2-butene	8.72E-11	Atkinson, 1986
b-pinene	7.81E-11	Atkinson, 1986
1,3-butadiene	6.66E-11	Atkinson, 1986
T2-butene	6.37E-11	Atkinson, 1986
T2-pentene	5.71E-11	Grosjean and Williams, 1992
C2-pentene	5.71E-11	Grosjean and Williams, 1992
C2-butene	5.60E-11	Atkinson, 1986
a-pinene	5.33E-11	Atkinson, 1986
camphene	5.33E-11	Atkinson, 1986
styrene	5.30E-11	Chiorboli et al., 1983
pinonaldehyde	4.00E-11	Davis et al., 2007
hexene	3.70E-11	Grosjean and Williams, 1992
ethyl vinyl ketone	3.60E-11	Grosjean and Williams, 1992
3-methyl-1-butene	3.17E-11	Atkinson, 1986
1-butene	3.11E-11	Atkinson, 1986
MVK+MACR	3.00E-11	Atkinson, 1986
1-pentene	2.74E-11	McGillen et al., 2007
propene	2.60E-11	Atkinson, 1986
m-xylene	2.45E-11	Atkinson, 1986
NO	1.53E-11	Atkinson et al 2004
p-xvlene	1.52E-11	Atkinson, 1986
acetaldehyde	1.50E-11	Zhu et al., 2008
mglvox	1.50E-11	Atkinson et al., 1997
o-xylene	1.47E-11	Atkinson, 1986
nopinone	1.43E-11	Atkinson and Aschmann, 1993
dodecane	1.32E-11	Atkinson, 2003
undecane	1.23E-11	Atkinson, 2003
NO2	1.20E-11	Atkinson et al., 2004
nonane	9.70E-12	Atkinson, 2003
formaldehyde	9.38E-12	Atkinson et al., 2001
ethylene	8.51E-12	Atkinson, 1986
octane	8.11E-12	Atkinson, 2003
ethylbenzene	7.51E-12	Atkinson, 1986
1-butyne	7.27E-12	Boodaghians et al., 1987
cyclohexane	6.97E-12	Atkinson, 2003
2-methylhexane	6.69E-12	Sprengnether et al., 2009
2,3,4-trimethylpentane	6.50E-12	Wilson et al., 2006
2,3-dimethylpentane	6.46E-12	Wilson et al., 2006
toluene	6.16E-12	Atkinson, 1986
2,4-dimethylpentane	5.48E-12	Baulch et al., 1986
2-methylpentane	5.20E-12	Atkinson, 2003
hexane	5.20E-12	Atkinson, 2003
pentane	3.84E-12	Atkinson, 2003
2,2,3-trimethylbutane	3.81E-12	Atkinson, 2003
n-butane	2.36E-12	Atkinson, 2003
2,2-dimethylbutane	2.23E-12	Atkinson, 2003
butiric acid	1.79E-12	Zetzsch, C. and Stuhl, F 1982
benzene	1.28E-12	Atkinson, 1986

methyl ethyl ketone	1.20E-12	Atkinson et al., 2001
propionic acid	1.20E-12	Atkinson et al., 2001
propane	1.09E-12	Atkinson, 2003
methanol	9.00E-13	Dillon et al., 2005
2,2-dimethylpropane	8.40E-13	Atkinson, 2003
acetic acid	8.00E-13	Atkinson et al., 2001
acetilene	7.79E-13	Atkinson, 1986
formic acid	4.50E-13	Atkinson et al., 2001
ethane	2.41E-13	Atkinson et al., 2001
acetone	1.80E-13	Raff et al., 2005
СО	1.44E-13	Atkinson et al., 1986
acetonitrile	2.20E-14	Atkinson et al., 2001
methane	6.40E-15	Vaghjiani and Ravishankara, 1991.

2) (i) Authors should discuss the potential influence of the boundary layer dynamics on the diurnal variability of OH reactivity, if any? Was the site above the nocturnal boundary layer?

(ii) The boundary layer height was only measured at a site near Bastia (about 50 km away from our measurement site), where it was about 400 m with some small fluctuations <100 m. However, these data are not completely representative for the site where the OH reactivity was measured, since it was influenced also by the proximity to the sea. Measurements of Rn-222 are available from the same site of measurements than the OH reactivity. This tracer can be used to estimate the variability of the boundary layer height (e.g. Chambers et al., 2015 and Karstens et al., 2015). Such estimates do not show a diurnal variability for the boundary layer to explain a connection with the variability of the OH reactivity. Due to the difficulty in interpreting the data of Radon, and to make a correct estimate of the BL height from the cited literature we did not consider this information as robust enough to include it in the discussion.

3) (i) Please mention whether the back trajectories consistent with the local wind direction measurements?

(ii) Yes, the back-trajectories were compared to wind roses for each cluster of data and showed a good consistency with the origin of the sector of the clusters.

Table 2: (i) LOD for GHG and CO measurements is missing

(ii) It is in the ppbv range. The information is added in the table.

Fig 4: (i) AVOCs % contribution is not legible; How were day and night time hours chosen?

(ii) The caption is modified and % are specified there as well. Daytime data were collected between 07.30 and 19.30 while nighttime data were between 19.30 and 07.30. This allowed to have at least three data points for the nighttime intervals since the calculated reactivity had a time resolution of three hours. This information is included in the caption as well.

(iii) Figure 4. Daytime (left pie) and nighttime (right pie) contributions of the measured compounds to the calculated OH reactivity. Daytime data were collected between 07.30 and 19.30 while nighttime data were between 19.30 and 07.30. Summed OH reactivity during daytime was maximum 11 s⁻¹, on average 4 ± 2 s⁻¹; while during nighttime it was maximum 3 s⁻¹, on average

2±0.4 s⁻¹. BVOCs (green), AVOCs (blue), OVOCs (orange) and others (red) stand for biogenic, anthropogenic, oxygenated volatile organic compounds and carbon monoxide and nitrogen oxides, respectively. During daytime, BVOCs, AVOCs, OVOCs and others contribution were 45%, 12%, 19%, 24%, respectively; while it was 7%, 23%, 27%, 43%, respectively during nighttime.

Page 11; Lines 27-30: (i) Please report the rate constants correctly. "x or E" is missing

(ii) Thanks, they have been corrected.

(iii) 3.6 x 10^{-10} cm³ molecule⁻¹ s⁻¹, see Atkinson, (1986) and Lee et al., (2006), more than three-fold higher than the one of the reactive isoprene ($k_{isoprene+OH}=1 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, Atkinson, 1986).

Page 13: (i) Not clear what is meant here...

"We considered a number of relevant monoterpenes emitted by Mediterranean 12 shrubs, including rosemary which was abundantly surrounding our monitoring station and 13 determined a rosemary-terpenes weighted reaction rate coefficient with OH of 1.56 10-10 cm3 14 molecule-1 s-1 (Bracho-Nunez et al., 2011)."

(ii) The meaning is that for the monoterpene reactivity we considered a weighted rate constant with OH accounting for different monoterpenes that are emitted by the Mediterranean maquis surrounding our measuring site. The sentence has been rephrased in the manuscript.

(iii) We roughly estimated how much OH reactivity can result from unmeasured monoterpenes: a number of monoterpenes emitted by Mediterranean plants surrounding the monitoring station was considered and a weighted reaction rate coefficient with OH of 1.56 10^{-10} cm³ molecule⁻¹ s⁻¹ was determined from them (see rosemary from Bracho-Nunez et al., 2011).

(i)Last line is not clear, please make it quantitative: "Our results demonstrate the relatively-high observed reactivity and the large impact of biogenic compounds"

(ii) The referee is right and the whole section about the missing reactivity and conclusion have been rewritten to clarify it.

(i)Page 4; Line 2: Suggest replacing "....makes a powerful means..." by "is a powerful means..." Page 6; Equation 2; Xi is missing , only i has been typed

(ii) We thank the reviewer. The text has been modified.

(iii)

$$R = \sum_{i} k_{i+OH} \cdot X_i \tag{2}$$

With *i* being any measured compound listed in Table 1 and X its concentration.

(i)Section 3.2.2: Please mention the efficiency of the photolytic converter used in the NOx analyzer

(ii) The efficiency of the conversion was 86%, this information has been added to the text.

(iii) NO_2 is quantified indirectly after being photolytically converted to NO (conversion efficiency=86%).

(i)Page 8; Line 14: "Measurements are corrected for H2O dilution to calculate the molar fractions in dry air": Please explain how as there are a number of ways that have been reported in the literature

(ii) Yes, here measurements were corrected for an empirical correction which takes into account the dilution effect and pressure broadening effect. A humidifying bench was developed to humidify a certified concentration of a gas stream at different humidity levels (see Rella et al., 2013). The sentence is rephrased and the new reference added.

(iii) Measurements were corrected for an empirical correction which takes into account the dilution effect and pressure broadening effect. A humidifying bench was developed to humidify a certified concentration of a gas stream at different humidity levels (see Rella et al., 2013).

Rella, C. W., Chen, H., Andrews, A. E., Filges, A., Gerbig, C., Hatakka, J., Karion, A., Miles, N. L., Richardson, S. J., Steinbacher, M., Sweeney, C., Wastine, B., and Zellweger, C.: High accuracy measurements of dry mole fractions of carbon dioxide and methane in humid air, Atmos. Meas. Tech., 6, 837-860, doi:10.5194/amt-6-837-2013, 2013.

(i)Page 8, Line 17: "Here" is used twice

Page 18; Line 19; Reference Paatero has a typo

Page 12; Line 23: throughout has been spelt as "through"

Page 12; Line28: Should be adsorbent instead of adsorbant

Page 13; Line 8: Typo in spelling of abundantly

Page 13; Line 32: Please correct the incorrect english phrase : "....associated to its formation..."

(ii) Done, thank you.

(i)Page 11: Line 14and later on as well: What is alpha terpinene? Terpinenes are a class of compounds. Do you mean alpha pinene?

(ii) Alpha-terpinene is a terpinene, known also as 1-Isopropyl-4-methyl-1,3-cyclohexadiene, it has the empirical formula C10H16 (http://www.sigmaaldrich.com/catalog/product/aldrich/86473?lang=it®ion=IT).

(i) Page 15; Line 23: Please correct english : "...associated to an increase....."

(ii) Done, thank you.

Summary:

(i)I suggest replacing "...technologies" by "... techniques".

(ii)Ok.