We thank anonymous referee (1) for the time he/she dedicated in reading and revising the manuscript and for the proposed suggestions to improve the manuscript quality.

Anonymous referee (1)

The manuscript presents OH reactivity measurements from a receptor site in the Western Mediterranean. OH reactivity represents an important top-down constraint on the amount of (OH) reactive species, which is directly relevant to radical cycling. At this site, which has low anthropogenic influence the OH reactivity furthermore mainly reflects the reactivity of biogenic volatile organic compounds (BVOCs) and their oxidation products. Important is also that the site has high terpene/isoprene ratios with a large contribution of alpha-terpinene, likely distinct from other sites for which OH reactivity has been reported. The manuscript thus presents a valuable data set providing insight into our understanding of contribution of BVOCs and their oxidation products to radical cycling. Two periods are identified that show larger discrepancies between the measured reactivity and that calculated from observed BVOCs and their reaction products. The work is an important addition to understanding the emission and fate reactive carbon in the atmosphere and should be published after the following comments have been addressed.

1. It would be very helpful to learn a little more about the OH reactivity measurement.

(a)

(i)How does the instrument sample the air and does this allow for observations of sesquiterpenes in the OH reactivity instrument or will they likely be lost. This is important for the comparison with calculated reactivity as sesquiterpenes were not observed.

(ii)The CRM sampled air through a 3 m long, 1/8'' OD PFA sampling line at a flow rate of 0.25 L/min with a residence time of the sample of 3 s. The sampling line was covered and kept at ambient temperature and installed at about 1.5 m above the trailer were the CRM was placed. We did not use any sampling pump before the reactor, but we used a PFTE filter at the inlet of the sampling line to avoid sampling particles. We think that the CRM was unable to sample sesquiterpenes due to losses on the walls of the sampling lines and/or on the filter surface. Sampling from CRM and GCs/PTR-MS instruments occurred within an area of about 100 m2. The sampling system for the PTR-MS consisted of a 5 m PFA sampling line, installed above the PTR-MS trailer (see Fig. 1). The line was covered and heated at 50°C. The residence time in the PTRMS sampling line was 4 s. The PTR-MS was operated at 1.33 mbar pressure and 40°C temperature of the drift tube for an E/N of 135 Td. Calibrations were performed every three days using certified gas mixtures including 15 VOCs (Restek, France), 9 VOCs (Praxair, USA), 9 OVOCs (Praxair, USA). More details on the calibration standards can be found in Michoud et al. (Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-955, in review, 2017). The PTR-MS may have sampled a fraction of the sesquiterpenes but did not detect them during the campaign. The Mediterranean maquis around the site is expected to emit sesquiterpenes but they were very likely lost before sampling due to their high reactivity in ambient air and due to adsorption in the sampling lines. We added a few remarks in the text.

(iii) page 5, line 25 please add:

Sampling was performed through a 3 m long, 1/8'' OD PFA sampling line at a flow rate of 0.25 sL/min with a residence time of the sample of 3 s. The sampling line was covered and kept at ambient temperature and installed at about 1.5 m above the trailer were the CRM was placed. We did not use any sampling pump before the reactor, but we used a PFTE filter at the inlet of the sampling line to avoid sampling particles. Some highly-reactive chemical species (i.e. sesquiterpenes) may have been lost before reaching the reactor due to wall losses in the sampling line and/or filter surface.

Line 5, page 7, please add:

Most of the chemical species used to calculate the OH reactivity were measured by PTR-MS and GC. The sampling system for the PTR-MS consisted of a 5 m PFA sampling line, installed above the PTR-MS trailer (see Fig. 1). The residence time in the sampling line was 4 s. The PTR-MS was operated at 1.33 mbar pressure and 40°C temperature of the drift tube for an E/N of 135 Td. The PTR was calibrated every 3 days using certified mixtures of different VOCs (15 VOCs from Restek, France, 9 VOCs from Praxair, USA, 9 OVOCs (Praxair, USA). More details on the calibration standards are available in Michoud et al. (2017). The GCs were calibrated twice at the beginning and at the end of the field campaign with certified gas mixtures: one including 29 VOCs (Praxair, USA), another including 29 NMHCs and three terpenes (NPL, UK).

(b)

(i)Definition of OH reactivity. There are a number of compounds in the atmosphere that after attack of OH can recycle OH rapidly. Probably the best known examples would be MACR, which recycles OH with a rate constant of 0.5 s-1 (Crounse et al. JPCA 116, 5756-5762, 2012, probably too slow to have an effect), isoprene hydroxyhydroperoxides forming isoprene epoxydiols, which likely recycle OH extremely fast, and RO2 that can recycle OH via reaction with HO2, (Praske et al. JPCA 119, 4562-4572, 2015, for example). Depending on the HO2 concentration in the instrument and the residence time, this could result in an underestimate of the actual OH reaction rate. It should be simple to model this, for the example of MVK+OH with the instrumental HO2 and residence time between OH addition and detection of pyrrole in the PTR.

(ii) OH recycling from unimolecular reactions such as the isomerization of peroxy radicals ($MACRRO_2$) produced during the OH oxidation of methacrolein is not expected to be significant due to the large concentrations of HO_2 in the CRM reactor. For instance, a HO_2 concentration of 10^{12} molecules/cm^3 would lead to a reaction rate of 14 s^{-1} for the reaction of $MACRRO_2$ with HO_2, which is significantly faster than the unimolecular isomerization rate of 0.5 s-1 for MACRRO2. In addition, $MACRRO_2$ will also react with other organic peroxy radicals present in the CRM reactor, especially peroxy radicals from pyrrole oxidation, reducing again the OH fraction recycled from $MACRRO_2$ isomerization. For the same reason, the impact of OH recycling from the isomerization of isoprene derived peroxy radicals is expected to be negligible.

OH recycling occurring when isoprene derived hydroxyhydroperoxide species (ISOPOOH) react with OH in the CRM reactor will effectively lead to an overestimation of the calculated reactivity since ISOPOOH can be mistaken for MVK+MACR and the measured OH reactivity does not reflect the neutrality of the ISOPOOH-OH reaction. ISOPOOH was not measured during the ChArMEx field campaign but Liu et al. (PNAS, 13, 6125-613, 2016) showed that the

ISOPOOH/(MVK+MACR) ratio ranges from 0.4-0.6 for the pristine area of the Amazon forest. This ratio is anticorrelated to NOy concentrations, which are very low in the Amazon forest. The NOx measured during our campaign were low as well, 600 pptv on average, therefore from the study of Liu and coworkers we can assume a range between 0-0.4 as an upper limit for ISOPOOH concentration in Corsica. During ChArMEx, [MVK+MACR] was 88 pptv on average, therefore we can assume [ISOPOOH] to be between 0-35 pptv. For such conditions, the calculated OH reactivity due to MVK+MACR would be overestimated of 0.03 s^{-1} on average.

Recycling of OH can also occur when acyl peroxy radicals react with HO_2. For instance Dillon and Crowley (ACP, 8, 4877-4889, 2008) measured an OH yield of 0.5 for the reaction between acetylperoxy (CH_3CO_3) and HO_2. CH_3CO_3 is produced in the CRM reactor during the OH-oxidation of acetaldehyde. The oxidation of higher aldehydes will also lead to acyl peroxy radicals that are likely capable of recycling OH. We investigated the impact of this chemistry on CRM measurements using the modeling methodology described in Michoud et al. (AMT, 8, 3537-3553, 2015). The simulations showed that the OH reactivity would be underestimated by approximately a factor of 2 for acetaldehyde. Measured acetaldehyde contributed to an OH reactivity of 0.12 s^{-1} on average during ChArMEx. Assuming an underestimation by a factor 2 for the OH reactivity due to acetaldehyde would lead to an underestimation of 0.06 s^{-1} on average. Concentrations of other aldehydes were lower than for acetaldehyde and the underestimation of the measured OH reactivity related to these compounds is expected to be negligible.

OH recycling from the reaction of other hydroxy-containing RO_2 radicals with HO_2 was also studied by Dillon and Crowley (ACP, 8, 4877-4889, 2008). The authors highlighted that OH was not a major product for the reaction, with an upper limit for the OH yield of 5-6%. An underestimation of the total OH reactivity from OH recycling from these species will therefore be negligible.
As a whole, the OH recycled by ISOPOOH and acetaldehyde would lead to a lower calculated reactivity by 0.03 s^{-1} and a higher measured reactivity of 0.06 s^{-1}. Since the measured OH reactivity was on average 5±4 s^{-1}, and the summed calculated OH reactivity was 3±2 s^{-1}, the recycling effects are negligible.

This is briefly commented in the manuscript.

(iii) Line 12, page 6:

The impact on CRM measurements of OH recycling reactions observed during the oxidation of some ambient species (e.g. methylvinylketone and methacrolein (MVK+MACR), isoprene hydroxyhydroperoxides (ISOPOOH), aldehydes) was determined to be negligible due to the low concentrations of these species and the high HO_2 concentration in the CRM reactor, which disfavor unimolecular reactions.

2. (i)P. 3 line 13: I did not see how this work "better elucidates the chemical processes, including ozone and secondary organic aerosol formation...over the Mediterranean basin". This requires more than comparing observed with calculated concentrations, i.e., a more quantitative framework addressing these chemical processes, ozone, SOA. I suggest removing this statement and simply

stating, what the very nice observational data at one specific location in the Mediterranean set actually shows, which is what the two bullet points do.

(ii)The referee is right, this study provides some elements but they are not enough to better elucidate the complexity of the atmospheric chemical processes, which is not actually done in the article, so this sentence is removed from the manuscript.

(iii)Please, substitute line 13 p. 3 with: "In our study, we address the following scientific questions:"

3. There are too many references to work in preparation.

(a)

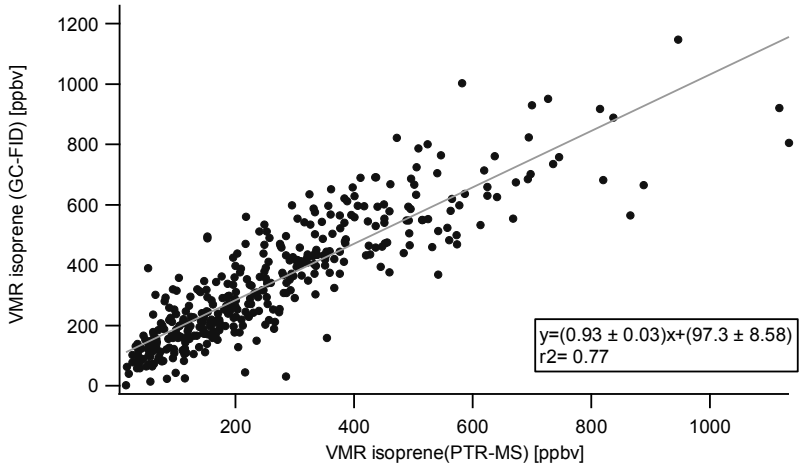
(i) P. 12 line 27-30. The comparison GC and PTR has to be shown. It is mentioned that isoprene correlated well for the GC and PTR but they could be of by a large factor. This has to be shown in the manuscript.

In extension of this, how were the GC and PTR measurements calibrated? Uncertainty in these directly relates to uncertainty in calculated reactivity. Extending the section on the (O)VOC measurements would be very helpful to this end. How was the terpene reactivity calculated, was the speciated one from the GC scaled up to give the same total as the PTR measurement?

I also recommend extending table 1, to include the rate constants used.

(ii) GC and PTRMS measurements were compared for isoprene and monoterpenes. The regression between the measurements of isoprene is reported in Fig 2 included in the supplementary material, a comment is also added in the text.

Figure 2 (supplement):



Most of the chemical species used to calculate the OH reactivity were measured by PTR-MS and GC. The sampling system for the PTR-MS consisted of a 5 m PFA sampling line, installed above the PTR-MS trailer (see Fig. 1). The residence time in the sampling line was 4 s. The PTR-MS was operated at 1.33 mbar pressure and 40°C temperature of the drift tube for an E/N of 135 Td. The PTR was calibrated every 3 days using certified mixtures of different VOCs (15 VOCs from

Restek, France, 9 VOCs from Praxair, USA, 9 OVOCs (Praxair, USA). More details on the calibration standards are available in Michoud et al. (2017). The GCs were calibrated twice at the beginning and at the end of the field campaign with certified gas mixtures: one including 29 VOCs (Praxair, USA), another including 29 NMHCs and three terpenes (NPL, UK).

Total uncertainties from measurements (including precision and calibration procedure) were in the range 5-23% for compounds measured by PTR-MS and GC-FID, and in the range 5-14% for GC-MS.

The monoterpenes OH reactivity was calculated using the speciated GC measurements, the concentrations were not scaled up to match the PTRMS measurements (sum of monoterpenes).

The referee is right, section 3.2 is extended including more information of VOCs measurements and an extended version of table 1 is included in the supplementary material.

(iii) Page 7 line 7, please add:

Most of the chemical species used to calculate the OH reactivity were measured by PTR-MS and GC. The sampling system for the PTR-MS consisted of a 5 m PFA sampling line, installed above the PTR-MS trailer (see Fig. 1). The residence time in the sampling line was 4 s. The PTR-MS was operated at 1.33 mbar pressure and 40°C temperature of the drift tube for an E/N of 135 Td. The PTR was calibrated every 3 days using certified mixtures of different VOCs (15 VOCs from Restek, France, 9 VOCs from Praxair, USA, 9 OVOCs (Praxair, USA). More details on the calibration standards are available in Michoud et al. (2017). The GCs were calibrated twice at the beginning and at the end of the field campaign with certified gas mixtures: one including 29 VOCs (Praxair, USA), another including 29 NMHCs and three terpenes (NPL, UK). Total uncertainties from measurements (including precision and calibration procedure) were in the range 5-23% for compounds measured by PTR-MS and GC-FID, and in the range 5-14% for GC-MS.

Page 13 line 22

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.

Page 14 line 2

Here, the summed calculated OH reactivity is obtained from data of isoprene and monoterpenes measured by GC.

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., 1982
pinonaldehyde	4.00E-11	Davis et al., 2007
hexane	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-xylene	1.52E-11	Atkinson, 1986
acetaldehyde	1.50E-11	Zhu et al., 2008
mglyox	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
acetylene	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
CO	1.44E-13	Atkinson et al., 1976
acetonitrile	2.20E-14	Atkinson et al., 2001
methane	6.40E-15	Vaghjiani and Ravishankara, 1991.

(b)

(i) More importantly, I recommend removing the PMF factorization aspect from the manuscript. As the actual PMF factorization is not presented it is impossible to evaluate this. For example, how high is the covariance between these factors, or in other words, in how far are these factors significant. I also think that this section is speculative and does not add much value to the manuscript. For example, it is stated that the first period (23/7-27/7) is "dominated" by OVOCs, referring to figure 2. Inspection of figure 2, to me, does not show any such dominance. In fact, to me it looks like the primary BVOCs dominate during the day, but I could be wrong. I also don't see how such a clear distinction as is made in the manuscript that the first period discrepancy is caused by "higher oxygenated chemicals" and for the second period by "oxidation products of BVOCs" is possible. This again requires a much more quantitative framework than presented here. The conclusion section thus is not very conclusive but rather has a lot of speculation. This does not detract from the importance of the observational data set and comparison with calculated reactivity.

(ii) The comparison between OH reactivity and PMF factors as presented in the manuscript is indeed not at its best supported by literature and explanations. However, the PMF study adds more elements of comparison with the OH reactivity and offers an original alternative to look into these type of datasets. For this reason we prefer to keep the analysis but we modified the section in order to make the study more robust and less speculative.

For the PMF factorization, the optimal solution was found after performing the PMF for different numbers of factors from 3 to 12. The best solution was finally retained regarding the residual, the rotational ambiguity and the minimum correlation between factor contributions in order to find the most independent factors.

Figure 8 is modified to show the PMF factors and OH reactivity datasets, including the primary biogenic factor – instead of the ln (ethane/propane) plot - indicating the component of the primary compounds emitted by biogenic sources as significant.

More information of PMF analysis are provided and additional information are available in the work of Michoud et al., now in review in ACPD (doi:10.5194/acp-2016-955).

Additionally, it is true, as the reviewer noticed that OVOCs contribution to the calculated OH reactivity dominates over BVOCs during the first period (23/07-27/07). OVOCs and BVOCs diel contributions are similar (27% and 26% respectively) but BVOCs dominates during daytime (38% against 24%). We thank the referee also for the next comment. It is not possible to differentiate among oxidation products of BVOCs and higher oxygenated chemicals from the elements provided. We show however a number of elements to support the idea that oxidation products play an important role in the missing reactivity during both periods.

The whole section has been rewritten.

(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.

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

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:

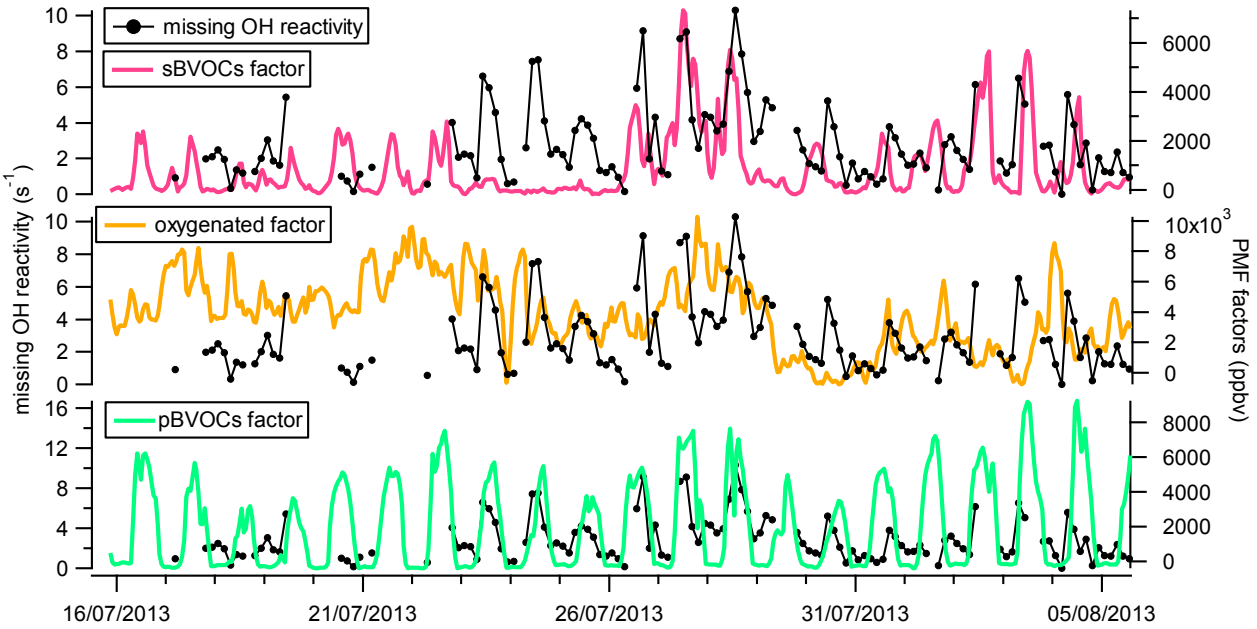


Figure 8. Time series of missing OH reactivity (left axis) reported with the factors obtained from positive matrix factorization analysis (right axis): primary-emitted biogenic volatile organic compounds factor (pBVOCs), oxygenated volatile organic compounds factor and secondary biogenic volatile organic 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} cm^3 $molecule^{-1}$ 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/z* 113 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/z* 71, *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 3-carene (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, $\beta = 0.11\ K^{-1}$, with a correlation coefficient of $R^2=0.92$. 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 $\beta = 0.173\ K^{-1}$ and $R^2=0.568$ 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 representing 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 with the missing OH reactivity. A clear influence on the missing OH reactivity is given by all 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} (1σ) 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., 2006, Sinha et al., 2010 and Noelscher et al., 2013). 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 photo-oxidation 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 23rd-27th).

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.

4. (i) p. 10 line 1 and line 17-19: The measured reactivity peaks around 16:00. However, no calculated contribution peaks at that time but rather around 14:00, hence the statement that the OH reactivity diurnal profiles resembles the one of the BVOC OH reactivity, which is significantly lower at 16:00 is not correct. This lag in the shape of the OH reactivity with respect to BVOCs, could lend support to oxidation products being important, which typically build up during the day, unless they are very short lived.

(ii) We thank the referee for this observation. It is true, the OH reactivity has a diurnal profile but it does not agree with none of the profiles from the calculated reactivity. Also, it can support the importance of unmeasured oxygenated products. This sentence is modified in the text.

(iii) Page 11, line 13, please add:

Here, the shape of the diurnal pattern of the measured reactivity is slightly shifted to the BVOCs OH reactivity, which might suggest the influence of oxidation products of biogenic molecules.

Additional/technical comments:

(i)

P. 1 line 27 “inferred” I would say that “calculated” from measured reactive gases. Inferred to me sounds like a vague, estimated process, but it is actually calculated here.

P. 2 line 3 “the biogenic volatile compounds” I assume this means with the reactivity calculated from the concentrations of biogenic VOCs. As written it is vague and could mean concentration of

BVOCs, which probably is not ideal, as different BVOCs have different diurnal profiles, as pointed out in the manuscript.

p. 2 line 5 associated respectively “with” instead of “to”

p. 2 line 7. biogenic “gas” not “gases”

p.2 line 7 delete “the” before “missing”

p.2 line 14: typically I see volatile organic compounds written in lower case, even if explaining the acronym.

p. 2 line 17 “all reactive compounds”, strictly “compounds reactive with OH”

p. 2 line 18 product “of” not “between”

p. 2 line 25 associated “with”

p.2 line 26 delete “either” before “secondary generated”

p. 2 line 28. I don’t think Portugal has a shore line on the Mediterranean, rather the strait of Gibraltar defines the western end of it, but I could be wrong.

p. 3 line 1-2. Is it relevant afterward in the manuscript that these species have not been identified anywhere else? It seems out of context.

p. 3 line 6, delete “a”

p.3 line 10-12: I am not sure that one paper proves this. Other regions of the world are even less sampled. I would suggest rephrasing as that additional observations are useful, but a minor point.

P. 3 line 18 “site” not “side”

P. 3 line 27 “local anthropogenic pollutants” is a little vague. Does it mean the same compounds could be coming from somewhere else?

P. 4 line 19: “measurements of gases and aerosol properties over a total surface area of ~ 100 square meters”. Please clarify, you measured the species across the whole area and nowhere else or the instruments were distributed over this area?

p. 8 line 17: “Here,...here”

p. 9 line 16 either “maximum” or “peak”

p. 9 line 31: To me the reactivity in figure 3 looks as it goes to about 4s-1 but not below 3s-1 at night.

P. 10 line 22: delete “to” in front of “the largest fraction”

P. 10 line 26 “larger” than what or simply state “large”

P. 11 line 18: Is it true that monoterpenes in all plant species have only-temperature dependent emission?

P. 11 line 14-30. It would be very helpful to have references to all reaction rate constants used for the calculated reactivities (I may have missed this, and apologize if I did).

P. 11 line 26: I do not understand the “hence” used here

P. 12 line 7. Perhaps clarify how the discrepancy is calculated, i.e.., calculated was 56% lower than measured, was 56% of measured, or measured was 56% higher than calculated etc.

P. 12 line 15: On the other “hand”

P. 12 line 16 “of “ the wind sector

P. 12 line 22-23. Again, at least during the day BVOCs dominate OVOCs, so statement as made, does not seem accurate.

p. 13 line 9: “or” monoterpenes.

p. 13 line 17-18: “Figure 6 shows the variability of the volume mixing ratios of BVOCs and oxidation products with local drivers such as temperature...”

P. 14 line 2 “effective” What does it mean for wind speed to be effective for monoterpernes?

P. 14 line 5 “small” instead of “little”

P. 17 line 11: Perhaps the term “secondary biogenic VOCs” could be redefined as it is a little unusual.

Figure 2: Does others not include methane, which probably contributes around 0.3 s-1.

Figure 3: Please add a total calculated reactivity trace, which would be very helpful.

Figure 7: Please show the same for the second period.

Lastly, the manuscript may benefit from language editing by a native speaker, if this is possible.

(ii) All comments were taken into account in the text and figures, we are very thankful to referee for the suggested edits. In figure 2 “others” refer only to CO and NOx.

Figure 3:

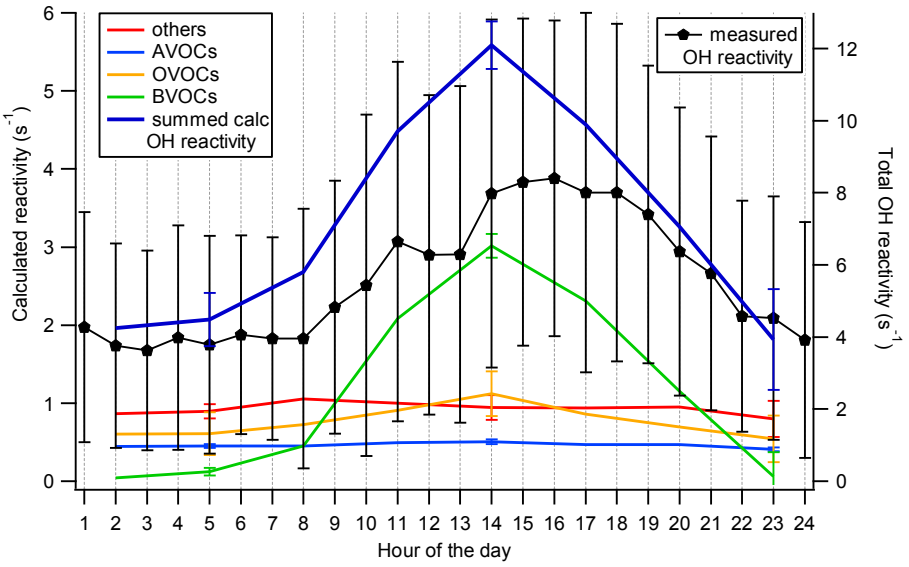


Figure 3. Diurnal patterns of measured (value with ±1σ, right axis) and calculated OH reactivity (left axis). Others, AVOCs, OVOCs, BVOCs are the contribution of CO and NOx (others), anthropogenic volatiles, oxygenated volatiles and biogenic volatiles to the summed calculated OH reactivity.

Figure 7:

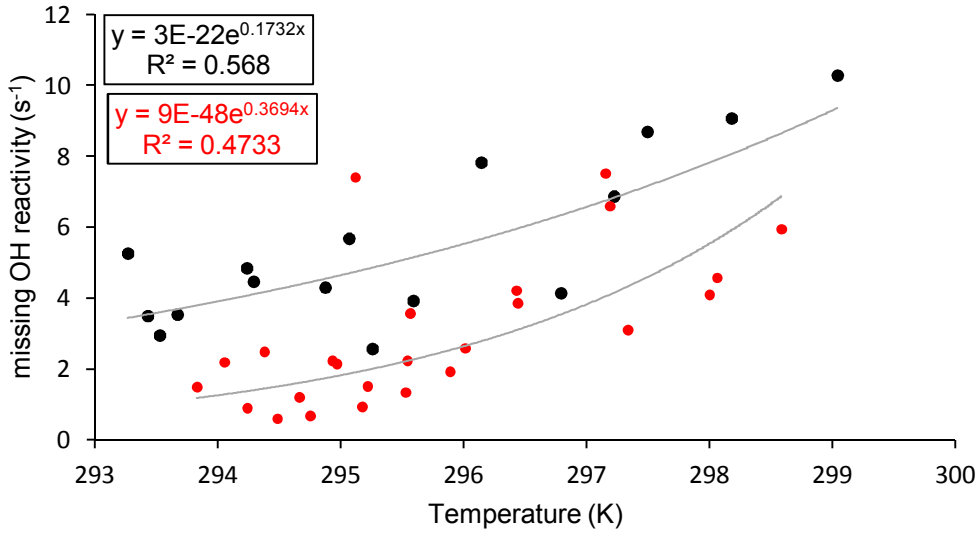


Figure 7. The difference between measured and calculated reactivity (missing OH reactivity) during July 23rd -26th July (red data points) and during July 27th -30th (black data points), dependence to temperature. The missing OH reactivity is fitted to E(T)=E(293) exp(β(T-293)), with β=0.37 K^{-1} and R^2=0.47 during July 23rd -26th July and β=0.17 K^{-1} and R^2=0.57 during July 27th -30th.

(iii) Please consider the final version of the manuscript for the technical edits.