

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 where the CRM was placed. We did not use any sampling pump before the reactor, but we used a PTFE 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 where the CRM was placed. We did not use any sampling pump before the reactor, but we used a PTFE 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 (MACRRO₂) produced during the OH oxidation of methacrolein is not expected to be significant due to the large concentrations of HO₂ in the CRM reactor. For instance, a HO₂ concentration of 10¹² molecules/cm³ would lead to a reaction rate of 14 s⁻¹ for the reaction of MACRRO₂ with HO₂, which is significantly faster than the unimolecular isomerization rate of 0.5 s⁻¹ for MACRRO₂. In addition, MACRRO₂ 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 MACRRO₂ 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 NO_y concentrations, which are very low in the Amazon forest. The NO_x 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 HO₂. For instance Dillon and Crowley (ACP, 8, 4877-4889, 2008) measured an OH yield of 0.5 for the reaction between acetylperoxy (CH₃CO₃) and HO₂. CH₃CO₃ 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 RO₂ radicals with HO₂ 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 HO₂ 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)

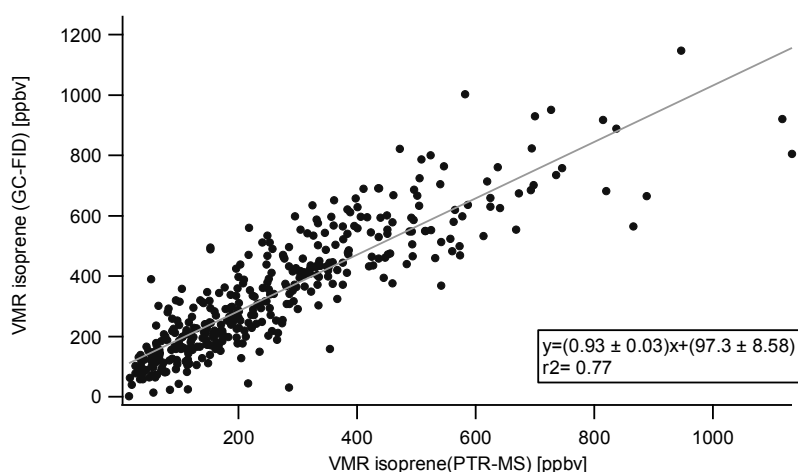
(i) P. 12 line 27-30. The comparison GC and PTR has to be shown. It is mentioned that isoprene correlated well for the GC and PTR but they could be off by a large factor. This has to be shown in the manuscript.

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} ($\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$)	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.

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

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:

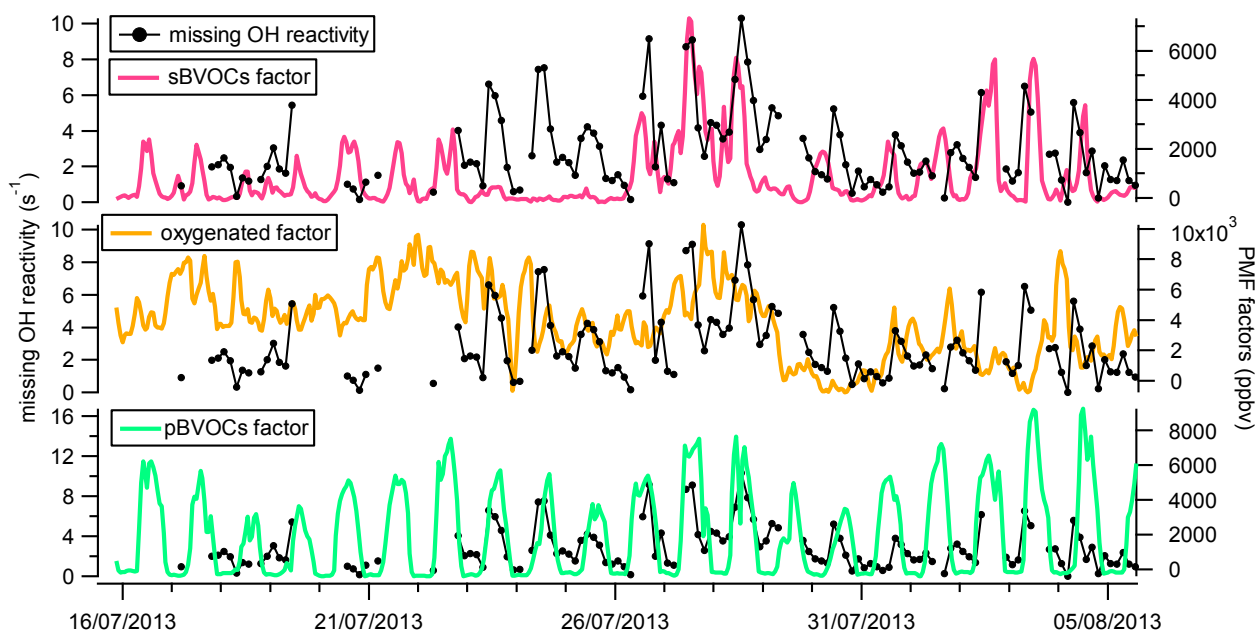


Figure 8. Time series of missing OH reactivity (left axis) reported with the factors obtained from positive matrix factorization analysis (right axis): primary-emitted biogenic volatile organic compounds factor (pBVOCs), oxygenated volatile organic compounds factor and secondary biogenic volatile organic 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 $1.56 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 $0.8\text{-}2.3 \text{ s}^{-1}$ 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 $E(T) = E(T_s) \exp[\beta(T - T_s)]$, where $E(T_s)$ is the emission rate at T_s , 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, $\beta = 0.11 \text{ K}^{-1}$, 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 $\beta = 0.173 \text{ K}^{-1}$ 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 significantly 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 $5 \pm 4 \text{ s}^{-1}$ (1σ) with a maximum value of $17 \pm 6 \text{ s}^{-1}$ (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 ($\sim 10 \text{ s}^{-1}$). 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 monoterpenes?

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:

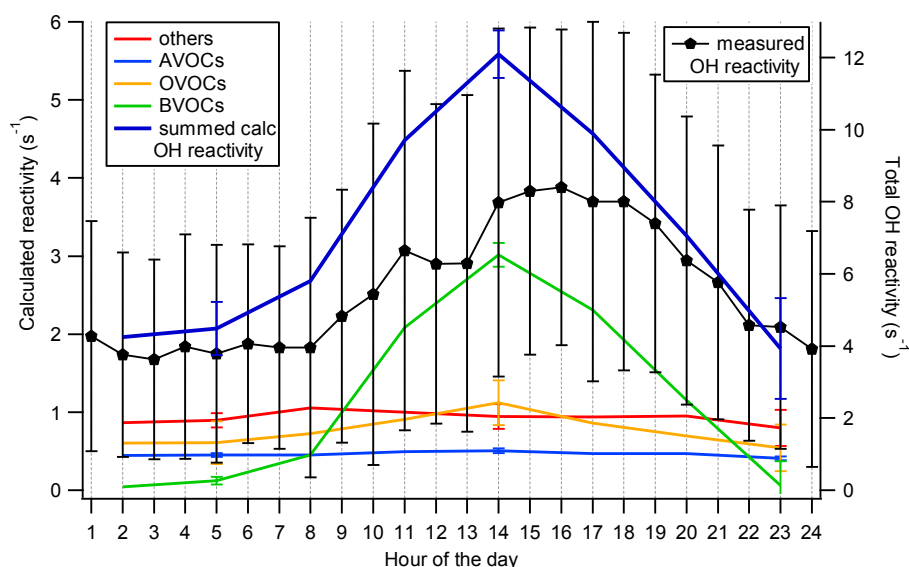


Figure 3. Diurnal patterns of measured (value with $\pm 1\sigma$, right axis) and calculated OH reactivity (left axis). Others, AVOCs, OVOCs, BVOCs are the contribution of CO and NO_x (others), anthropogenic volatiles, oxygenated volatiles and biogenic volatiles to the summed calculated OH reactivity.

Figure 7:

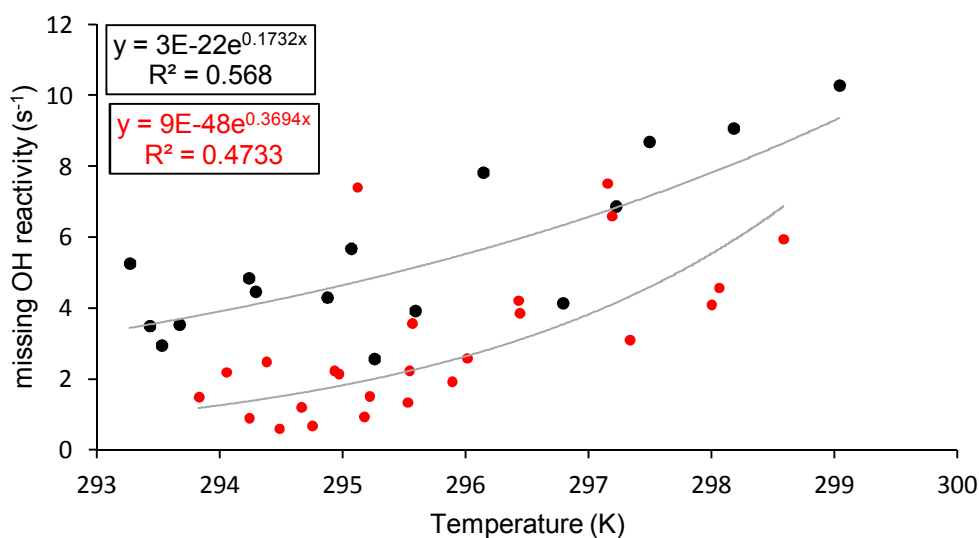


Figure 7. The difference between measured and calculated reactivity (missing OH reactivity) during July 23rd -26th July (red data points) and during July 27th -30th (black data points), dependence to temperature. The missing OH reactivity is fitted to $E(T)=E(293) \exp(\beta(T-293))$, with $\beta=0.37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

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

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

Anonymous referee (2)

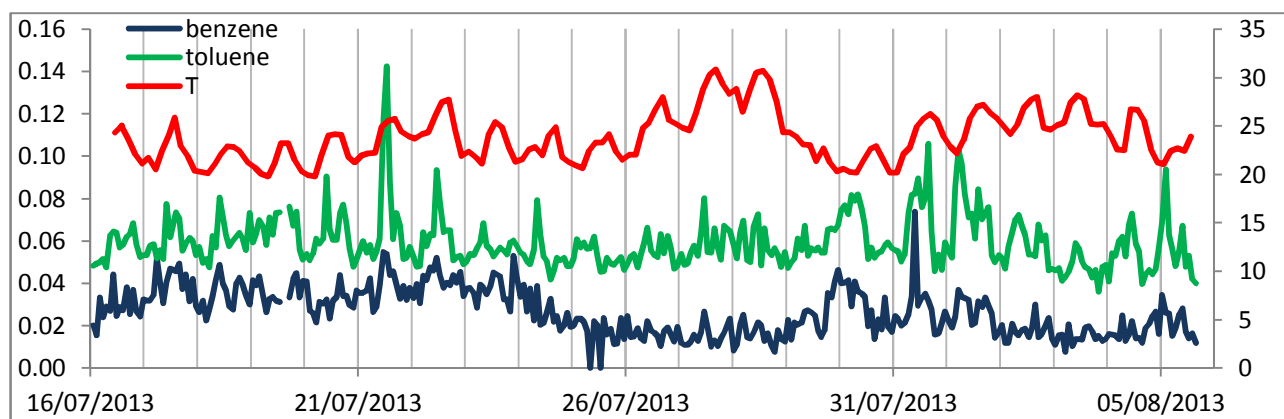
General comments:

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 CHARME 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. These findings are very interesting and the work will be a valuable addition to 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 (<http://www.atmos-chem-phys-discuss.net/acp-2016-955/>) 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.

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

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:

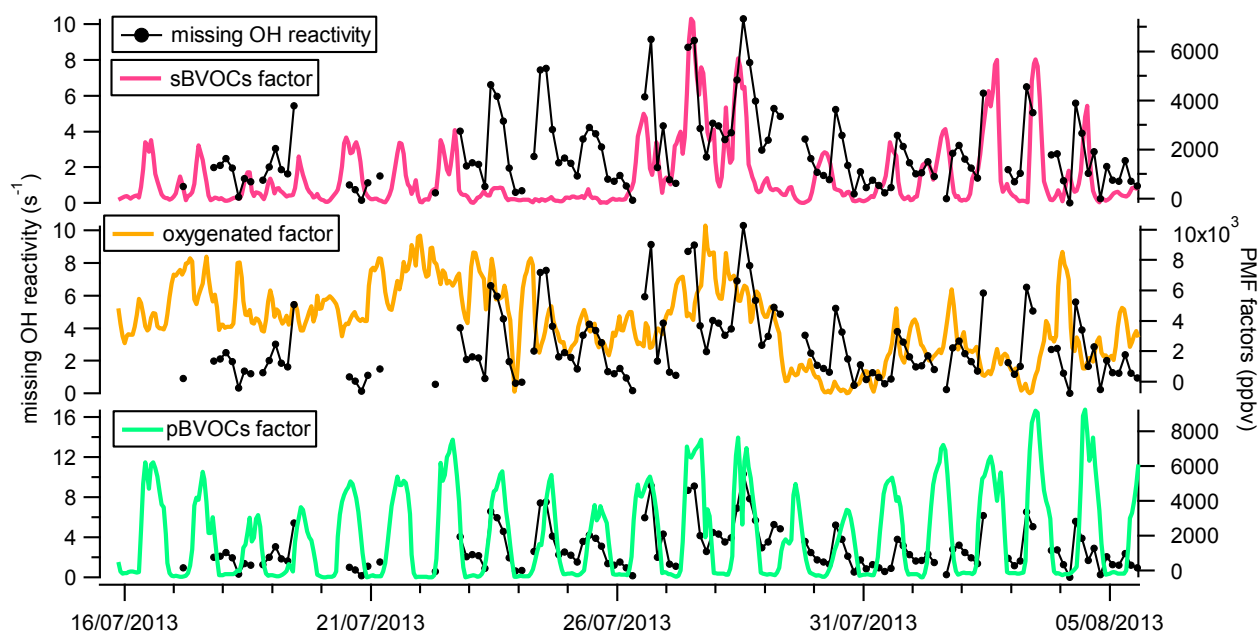


Figure 8. Time series of missing OH reactivity (left axis) reported with the factors obtained from positive matrix factorization analysis (right axis): primary-emitted biogenic volatile organic compounds factor (pBVOCs), oxygenated volatile organic compounds factor and secondary biogenic volatile organic 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 $1.56 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 $E(T) = E(T_s) \exp[\beta(T - T_s)]$, where $E(T_s)$ is the emission rate at T_s , 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, $\beta = 0.11 \text{ K}^{-1}$, 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 $\beta = 0.173 \text{ K}^{-1}$ 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 significantly 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 $5 \pm 4 \text{ s}^{-1}$ (1σ) with a maximum value of $17 \pm 6 \text{ s}^{-1}$ (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, 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 ($\sim 10 \text{ s}^{-1}$). 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.

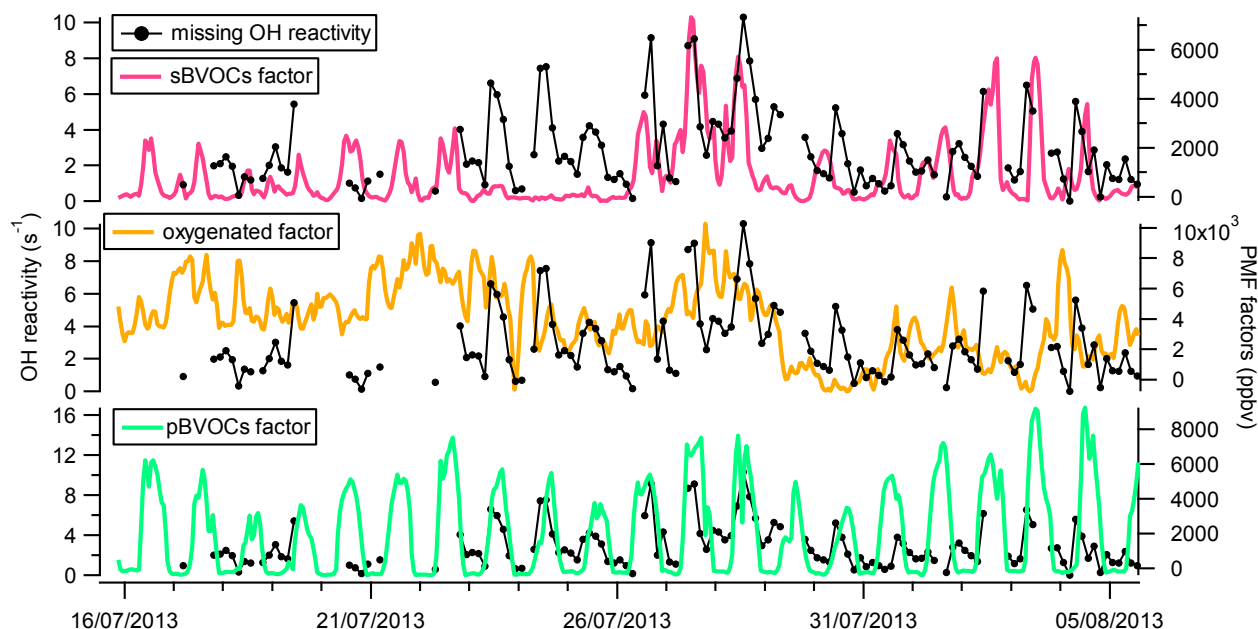
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Finally, as the Mediterranean basin differs from side to side, (air masses reception as well as type of ecosystems) more intensive studies at different key spots, e.g. western vs eastern basin and remote vs. periurban ecosystems, would be helpful for 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} ($\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$)	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-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
NO ₂	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., 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 $4 \pm 2 \text{ s}^{-1}$; while during nighttime it was maximum 3 s^{-1} , on average

$2 \pm 0.4 \text{ s}^{-1}$. 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) $3.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, see Atkinson, (1986) and Lee et al., (2006), more than three-fold higher than the one of the reactive isoprene ($k_{\text{isoprene}+\text{OH}} = 1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 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 $1.56 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (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 $1.56 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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; X_i is missing, only i has been typed

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

(iii)

$$R = \sum_i k_{i+\text{OH}} \cdot X_i \quad (2)$$

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 NO_x analyzer

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

(iii) NO₂ 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.

Summertime OH reactivity from a receptor coastal site in the Mediterranean basin

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Abstract

Total OH reactivity, the total loss frequency of the hydroxyl radical in ambient air, provides the total loading of OH reactants in air. We measured the total OH reactivity for the first time during summertime at a coastal receptor site located in the western Mediterranean basin. Measurements were performed at a temporary field site located in the northern cape of Corsica (France), during summer 2013 for the project CARBOSOR (CARBOn within continental pollution plumes: SOurces and Reactivity) -ChArMEx (Chemistry-Aerosols Mediterranean Experiment). Here, we compare the measured total OH reactivity with the OH reactivity **calculated** from the measured reactive gases. The difference between these two parameters is termed missing OH reactivity, i.e., the fraction of OH reactivity not explained by the measured compounds. The total OH reactivity at the site varied between the instrumental LoD (limit of detection= 3 s^{-1}) to a maximum of $17 \pm 6 \text{ s}^{-1}$ (35% uncertainty) and was $5 \pm 4 \text{ s}^{-1}$ (1σ standard deviation) on average. It varied with air temperature exhibiting a diurnal profile **comparable to the reactivity calculated from the concentration of the biogenic volatile organic compounds measured at the site**. **For part of the campaign, 56% of OH reactivity was unexplained by the measured OH reactants (missing reactivity)**. We suggest that oxygenated molecules formed mostly from reactions of biogenic **gas** precursors, were the major contributors to missing OH reactivity.

1 Introduction

Atmospheric photo-oxidation reactions are initiated by three main oxidants: the hydroxyl radical (OH), ozone (O₃) and the nitrate radical (NO₃). Among those, the OH radical is by far the most important, capable of reacting with the vast majority of chemical species in the troposphere (Levy, 1971). Photo-oxidation reactions are the most efficient cleansing processes occurring in the atmosphere, and constitute an important sink for reactive gases including volatile organic compounds (VOCs).

Total OH reactivity is the first-order total loss rate of the hydroxyl radical in the atmosphere due to reactive molecules. It is the total sink of OH, therefore representing a top-down measure of OH reactants present in ambient air.

Measurements of the total loss of OH and reactive gases are often coupled. The total reactivity of the latter is determined by summing each gas individual reactivity as the product of their atmospheric concentration and their reaction rate coefficient with OH. Here, this is referred to as calculated OH reactivity and comparisons between the calculated and the measured OH reactivity have showed that discrepancies in various environments and different proportions exist (di Carlo et al., 2004, Nölscher et al., 2016). The missing OH reactivity, namely the fraction of OH reactivity not explained by simultaneous measurements of reactive gases, has been associated with unmeasured compounds either primary emitted, secondary generated, or both (e.g. Sinha et al., 2010, Nölscher et al., 2012, Nölscher et al., 2013, Edwards et al., 2013, Hansen et al., 2014, Kaiser et al., 2016).

The Mediterranean basin comprises countries from three different continents and a population of 450 million inhabitants. Its climate is characterized by humid-cool winters to hot-dry summers, when the area is usually exposed to intense solar radiation and high temperatures. Forests, woodlands and shrubs occupy large areas of the region, which has rich biodiversity and is the habitat to a high number of identified species (Cuttelod et al., 2008). The dominant airflow in summertime is driven from North to South and the basin is exposed to air masses coming from European cities and industrialized areas. Therefore, transported pollution and the intense local anthropogenic and biogenic activity result in high loadings of atmospheric gases, particles and complex chemistry (Lelieveld, 2002).

Climate model predictions indicate that the Mediterranean area will face unique impacts of climate change. Predictions show that this region will suffer higher temperatures and extended drought periods, thus affecting the strength and type of emissions which will further impact air quality and climate (Giorgi and Lionello, 2008). Finally, additional observations are useful for better predicting the future state of this region (Mellouki and Ravishankara, 2007).

In this study, we address the following scientific questions:

- 1) What proportion of the total reactive gases emitted and formed over the area do we know and can we detect?
- 2) Which species mostly influence the OH reactivity over this site within the basin?

To answer these questions, we measured the total OH reactivity at a receptor coastal site in the western Mediterranean basin during summer 2013. Measurements were part of an intensive fieldwork campaign aimed at investigating sources and sinks of gaseous constituents in the area (CARBOSOR, CARBOn within continental pollution plumes: Sources and Reactivity, within the ChArMEx project, Chemistry and Aerosols in a Mediterranean Experiment; charmex website: <http://charmex.lsce.ipsl.fr/>). Total OH reactivity was measured with the comparative reactivity method instrument (CRM) (Sinha et al., 2008) during 16/07/2013-05/08/2013 at the monitoring station of Ersu, France. The field site was chosen for being: (i) far from anthropogenic sources; (ii) exposed to aged air masses of different origins, including air masses enriched in oxidation products transported from continental industrialized areas. Total OH reactivity here served to evaluate whether the ambient reactive gases were all identified or not. Specifically, we were able to determine what kind of pollution event could be better captured through the instrumentation deployed at the site, assuming that a group of reactive gases traces a specific type of event (primary anthropogenic or biogenic emissions, secondary formation). Due to the high number of existing VOCs, OH reactivity also makes a powerful means for investigating VOC emissions and reactions. Comparisons with a VOC factorial analysis and with a number of additional parameters provided crucial insights into the summertime reactive gases budget in this area of the western basin. The following sections will describe the field site under study, the methodologies used, our results of OH reactivity and insights into the unmeasured reactive gases.

2 Field site

The Ersu windfarm (42.97°N, 9.38°E, altitude 533 m) is located in the northern cape of Corsica (France), in the western Mediterranean basin (figure 1). It is 2.5 km away from the nearest coast (West side) and 50 km away from the largest closest city and harbour Bastia (South side). It is located on a hill (533 m a.s.l.) and it is surrounded by the Mediterranean Sea on West, North and East sides. The site was chosen for its peculiarities of receiving air masses from continental areas especially France and northern Italy, with the harbours of Marseille and Genoa about 300 km away, and the industrialized areas of Milan and the Po valley 400 km away. Furthermore, the measurement station is densely surrounded by the Mediterranean maquis, a shrubland biome typical of the whole Mediterranean region. The ground station consists of a long-term meteorology, trace gas concentrations, aerosol size, a composition monitoring laboratory (measurements collected from 2012 to 2014), and temporary measurements of gases and aerosol properties over a total surface area of ~100 square meters where instruments are distributed. Measurements of total OH reactivity and trace gases reported in this study were all performed within this area (see figure 1 for details).

We measured the OH reactivity during two main periods: an intercomparison exercise for OH reactivity between two CRM instruments during 8/07/2013-13/07/2013 (see Zannoni et al., 2015), and the intensive ambient monitoring campaign, CARBOSOR during 16/07/2013-05/08/2013. Within the same project, instruments for measuring radicals, inorganic and organic compounds, aerosol chemical composition and their physical properties, and meteorology were simultaneously deployed. The next section will provide an overview of the methods selected for this study.

3 Methods

3.1 Comparative Reactivity Method

We carried out measurements of total OH reactivity using a comparative reactivity method instrument assembled in our laboratory (CRM-LSCE from Laboratoire des Sciences du Climat et de l' Environnement, see Zannoni et al., 2015). In brief, the comparative reactivity method is based on the concept of producing a competition for in-situ generated OH radicals, between a reactive reference compound, in our case pyrrole (C_4H_5N), and ambient reactive gases (Sinha et al., 2008). This is achieved by introducing a known amount of pyrrole diluted in zero air and N_2 in a flow reactor coupled to a Proton Transfer Reaction-Mass Spectrometer (PTR-MS, see Lindinger et al., 1998, De Gouw and Warneke, 2007). Pyrrole is chosen as a reference compound for its well characterized kinetics (Atkinson et al., 1984, Dillon et al., 2012), for not being present in the atmosphere at normal conditions, and for being easily detectable at the protonated m/z 68 ($C_4H_5NH^+$) through PTR-MS without any interference. The Proton Transfer Reaction-Mass Spectrometer run at standard conditions ($P_{\text{drift}} = 2.2$ mbar, $E/N = 130$ Td ($1 \text{ Td} = 10^{-17} \text{ Vcm}^{-1}$), $T_{\text{inlet}} = 60$ °C) is the detector of choice for its real-time measurement capabilities and robustness over time (see also Nölscher et al., 2012b).

The CRM usual experimental procedure includes the following stages: monitoring of C0 wet/dry, followed by C1 dry or wet, C2 wet, and C3 ambient. With C0, C1, C2, C3 being the concentration of pyrrole detected with the PTR-MS, in order: after injection (C0), after photolysis of pyrrole (C1), after reaction with OH (C2), when ambient air is injected and the competition for OH radicals starts (C3). Switches between C2 (background pyrrole in zero air) and C3 (pyrrole in ambient air) result in modulations of the pyrrole signal which are used to derive total OH reactivity values from the following equation:

$$R_{\text{air}} = \frac{(C3 - C2)}{(C1 - C3)} \cdot k_{\text{pyrrole} + \text{OH}} \cdot C1 \quad (1)$$

With $k_{\text{pyrrole} + \text{OH}}$ being the rate constant of reaction between pyrrole and OH= $(1.20 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1984, Dillon et al., 2012).

During the whole campaign we ran systematic quality check controls on the instrument (see supplementary material).

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 where the CRM was placed. A PTFE filter was placed 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.

We recorded PTR-MS data using a dwell time of 20 s for pyrrole, with a full cycle of measurements every 30 s. We switched between C2 and C3 every 5 minutes, resulting in a data point of reactivity every 10 minutes. Each data point of reactivity obtained from eq. (1) was corrected for: (i) humidity

changes between C2 and C3, (ii) deviation from the assumption of pseudo first order kinetics between pyrrole and OH, (iii) dilution of ambient air reactivity inside the reactor. A detailed description on how the correction factors were obtained and how the raw data were processed can be found in the publication of Zannoni et al., (2015). We did not account for OH recycling in our reactor due to nitrogen oxides (NO+ NO₂) since ambient nitrogen monoxide (NO) was below 0.5 ppbv at the site (NO₂ below 2 ppbv), which is too low for interfering with the system. Tests performed in the laboratory after the campaign have demonstrated that the instrument is not subject to ozone interference. 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 HO₂ concentration in the CRM reactor, which disfavor unimolecular reactions.

The limit of detection (LoD) of CRM-LSCE was estimated to be $\sim 3 \text{ s}^{-1}$ (3σ) and the systematic uncertainty $\sim 35\%$ (1σ), including uncertainties on the rate coefficient between pyrrole and OH (8%), detector sensitivity changes and pyrrole standard concentration (22%), correction factor for kinetics regime (26%) and flows fluctuations (2%); see also Michoud et al., 2015. An intercomparison exercise with another CRM instrument carried out before the campaign demonstrated that the measured reactivities were in good agreement (linear least squares fit with a slope of one and R² value of 0.75).

3.2 Complementary measurements at the field site

Gaseous compounds were measured using a broad set of techniques available at the site, including: Proton Transfer Reaction-Mass Spectrometry (PTR-Time of Flight MS, Kore Technology Ltd., UK), online and offline Gas Chromatography (GC-FID/FID and GC-FID/MS, Perkin Elmer), Liquid Chromatography (HPLC-UV, High Performance Liquid Chromatography-UV light detector), for VOCs and oxygenated VOCs specifically; analysis based on the Hantzsch reaction method (AERO-LASER GmbH, Germany) for detecting formaldehyde; and wavelength-scanned cavity ring down spectrometer (WS-CRDS, G2401, Picarro, USA) for CO, CH₄ and CO₂. The measured concentration and the reaction rate coefficients of each measured compound with OH were used to calculate the OH reactivity with eq. (2):

$$R = \sum_i k_{i+OH} \cdot X_i \quad (2)$$

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

Most of the chemical species used to calculate the OH reactivity were measured through 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 (Restek, France), 9 VOCs (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.

We refer to the manuscript of Michoud et al.(2017), for a detailed description of the PTR-MS, online GC and offline sampling on adsorbent cartridges on GC-FID/MS deployed at the site; while the formaldehyde, NO_x, O₃ analysers and WS-CRDS are briefly introduced in the following sections. Table 2 provides a summary of all techniques.

3.2.1 Hantzsch method for measuring formaldehyde

Formaldehyde (HCHO) was measured with a commercial instrument based on the Hantzsch reaction (Model 4001, AERO-LASER GmbH, Germany). Gaseous HCHO is stripped into a slightly acidic solution, followed by reaction with the Hantzsch reagent, i.e. a diluted mixture of acetyl acetone acetic acid and ammonium acetate. This reaction produces a fluorescent compound which absorbs photons at 510 nm. More details are given in Dasgupta et al., (1988), Junkermann, (2009) and Preunkert et al., (2013).

Sampling was conducted through a 5 m long PTFE 1/4" OD line, with a 47 mm PFA in-line filter installed at the inlet and a flow rate of 1 L min⁻¹.

The liquid reagents (stripping solution and Hantzsch reagent) were prepared from analytical grade chemicals and ultrapure water according to the composition given by Nash, (1953) and stored at 4 °C on the field. The instrumental background was measured twice a day (using an external Hopcalite catalyst consisting of manganese and copper oxides) and calibrated three to four times a week using a liquid standard at 1.10⁻⁶ mol L⁻¹, i.e volume mixing ratio in the gaseous phase of about 16 ppbv. The calibration points were interpolated linearly in order to correct for sensitivity fluctuations of the instrument. The limit of detection was 130 pptv (2σ). The coefficient of variation, i.e the ratio of the standard deviation to the mean background value, was estimated to be 0.4 %. Measurements of HCHO ran smoothly from the beginning of the campaign until 11 AM LT (local time) of 28/07/2013. At this time an instrument failure occurred and measurements were stopped.

3.2.2 Chemiluminescence for measuring NO_x

A CRANOX instrument (Ecophysics, Switzerland) was used to measure nitrogen oxides (NO_x=NO+NO₂). The instrument is based on ozone chemiluminescence therefore it can directly measure NO. NO₂ is quantified indirectly after being photolytically converted to NO (conversion efficiency=86%). The instrument consists of a high performing two channel CLDs (Chemiluminescence Detectors) with pre-chambers background compensation, an integrated powerful pump, a photolytic converter, an ozone generator and a calibrator. A control software handles and manages the different tasks. The detection limit is 50 pptv (3σ), for a 5 minute time resolution.

3.2.3 Wavelength-scanned cavity ring down spectrometry (WS-CRDS) for measuring greenhouse gases

In-situ measurements of CO₂, CH₄, CO molar fractions at Ersa are part of the French monitoring network of greenhouse gases, integrated in the European Research Infrastructure ICOS (integrated

carbon observation system). The air is sampled at the top of a 40 m high telecommunication tower (573 m), and is analyzed with a wavelength-scanned cavity ring down spectrometer (WS-CRDS, G2401, Picarro, USA). The analyzer is calibrated every 3 weeks with a suite of four reference standard gases, whose molar fractions are linked to the WMO (World Meteorological Organization) scales through the LSCE (Laboratoire des Sciences du Climat et de l'Environnement) reference scale. 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).

3.3 Positive Matrix Factorization analysis

Positive Matrix Factorization (PMF) analysis was here performed using EPA (environmental protection agency) PMF 3.0 and the protocol proposed by Sauvage et al. (2009) on a dataset of 42 VOCs including, NMHCs (non-methane hydrocarbons) and OVOCs (oxygenated volatile organic compounds) and 329 observations (time resolution of 90 min). The data set is considered as an 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.

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

The optimal solution is found by 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 VOCs database of the CARBOSOR-ChArMEx campaign is available in Michoud et al., (2017).

3.4 Air masses back-trajectories

The back-trajectories of the air masses were modelled with Hysplit (HYbrid Single-Particle Lagrangian Integrated Trajectory developed by the National Oceanic and Atmosphere Administration (NOAA) Air Resources Laboratory (ARL) (Draxler and Hess, 1998, Stein et al., 2015) for 48 h every 6 hours.

The back-trajectories were grouped according to their origin, altitude and wind speed, such as: 1.North-East, 2.West, 3.South, 4.North-West and 5. Calm-low wind speed/stagnant conditions. More details on the air masses origin and their photochemical age is available in Michoud et al., (2017).

4 Results

4.1 Total measured OH reactivity

The 3-h averaged measured OH reactivity is represented by the black line in figure 2. Here, all data acquired during 16/07/2013- 05/08/2013 is reported, missing data points are due to minor instrumental issues and instrumental quality check controls. Figure 2 also shows the temperature profile of ambient air (gray line, right axis). The OH reactivity varied between the instrumental LoD (3 s^{-1}) to $17 \pm 6 \text{ s}^{-1}$ (3-h averaged maximum value $\pm 35\%$ uncertainty). From the 10 minute time resolution data the highest value of OH reactivity was 22 s^{-1} , reached on 28/07/2013 during the afternoon, when the air temperature at the site was also exhibiting its maximum. During the whole field campaign the average measured OH reactivity was $5 \pm 4 \text{ s}^{-1}$ (1σ). This value agrees with averaged values of OH reactivity collected during autumn 2011 in the South of Spain for southerly-marine enriched air masses (Sinha et al, 2012). In contrast, higher OH reactivity was measured during spring 2014 in a Mediterranean forest of downy oaks, where the average campaign value was $26 \pm 19 \text{ s}^{-1}$ and the maximum value was 69 s^{-1} (Zannoni et al., 2016).

OH reactivity and air temperature at the site in Corsica co-varied during the whole campaign, with highest values reached during daytime in the periods between 26-28/07/2013 and 02-03/08/2013. Figure 2 also reports the origin of the air masses reaching the field site. The dominant origin of the sampled air masses was West, indicating that air masses which had travelled over the sea being possibly more aged. It is not evident that the variability of the OH reactivity is affected by the origin of the air masses. In contrast, air temperature seems to have played a major role. Indeed, during the periods of highest reactivity, the origin of air was different, with air masses coming from the western to the southern and the north-eastern sectors. The diurnal pattern of OH reactivity for the whole campaign is reported in figure 3. Here it is evident that the background value was about 4 s^{-1} during nighttime, it increased at 8:00 AM LT, peaked at 11:00 AM LT, reached a second maximum at 4:00 PM LT and finally decreased at 7:00 PM LT to reach its background value at 10:00 PM LT (local time GMT/UTC+2 hours). It is worth noting that the large amplitude of standard deviation bars (1σ) highlights the large diel variability.

4.2 Calculated OH reactivity and BVOCs influence

Table 1 provides the number and type of chemical species measured at the same time and site as the OH reactivity. Their concentrations and reaction rate coefficients with OH were used to determine the calculated OH reactivity from eq. (2). A broad set of compounds were monitored at the site, herein classified as: anthropogenic volatile organic compounds (AVOCs, 44 compounds measured), biogenic volatile organic compounds (BVOCs, 7), oxygenated volatile organic compounds (OVOCs, 15) and others (3 species: CO, NO and NO₂). The reader can refer to table 1 for the classification of the chemical species adopted throughout the manuscript. Figure 2 shows the time series of the summed calculated OH reactivity (thick blue line) and the contributions of each class of chemicals. The maximum of the summed calculated OH reactivity was 11 s^{-1} , and the 24-h averaged value was $3 \pm 2 \text{ s}^{-1}$ (1σ). As represented in figure 3, the class of the biogenic compounds played an important role on the daytime OH reactivity. Here, the shape of the diurnal pattern of the measured reactivity is slightly shifted to the BVOCs OH reactivity, which suggests there is an

influence from the oxidation products of biogenic molecules. The mean percentage contribution of each class of compounds to the summed calculated reactivity is determined for daytime (from 07:30 to 19:30, LT) and nighttime data (from 19.30 to 04.30 LT) and is represented in figure 4. During daytime BVOCs contributed the largest fraction of OH reactivity (45%), followed by inorganic species (24%), OVOCs (19%) and finally AVOCs (12%). Interestingly, only 7 BVOCs had a higher impact than 44 AVOCs. This is explained by: i) the relatively high concentration of BVOCs (maximum values for isoprene and sum of monoterpenes is 1 and 1.5 ppbv, respectively), ii) the generally large BVOC reaction rate coefficients with OH (Atkinson and Arey, 2003) and iii) the relatively low concentration of AVOCs measured during the campaign. BVOCs accounted only for 5% of the total VOCs concentration, followed by AVOCs (15%) and OVOCs (79%) (the percentages are calculated from mean campaign values, see also Michoud et al., 2017) which highlights the reactive nature of the measured BVOCs. During nighttime, BVOCs concentrations decreased (see figures 2 and 3); CO and NO_x had the largest influence on OH reactivity (43%), followed by OVOCs (27%), AVOCs (23%) and BVOCs (7%). Particularly, CO and long-lived OVOCs and AVOCs constituted a background reactivity of $\sim 2\text{--}3\text{ s}^{-1}$, as also shown by the diurnal profiles reported in fig. 3.

Inside the BVOCs class, the total fraction of monoterpenes contributed more than isoprene to the OH reactivity (fig. 5). During daytime, OH reactivity due to monoterpenes was between $1.4\text{ to }7.4\text{ s}^{-1}$ and varied with air temperature, on the other hand, isoprene reactivity with OH varied between $0.3\text{--}2.3\text{ s}^{-1}$ (minimum and maximum values on 29/07/13 and 03/08/2013, respectively). In contrast with monoterpenes OH reactivity, the reactivity of isoprene towards OH varied with both air temperature and solar irradiance. Overall both monoterpenes and isoprene OH reactivities had the characteristic diurnal profile observed for their atmospheric concentrations. High concentrations depended on air temperature, solar radiation as well as calm-low wind speed conditions. These results indicate a large impact of BVOC oxidation on the local photochemistry.

The very reactive monoterpene α -terpinene had the largest contribution on OH reactivity among the measured BVOCs (31%), followed by isoprene (30%), β -pinene (17%), limonene (12%), α -pinene (8%), camphene (2%) and γ -terpinene (1%), over a total averaged daytime reactivity due to BVOCs of $2\pm 2\text{ s}^{-1}$ (1σ), see table 3. During the night, monoterpenes had a larger impact than isoprene due to their known temperature dependency (Kesselmeier and Staudt, 1999). α -terpinene was the most reactive-to-OH BVOC also during nighttime, see table 3. In terms of absolute values, α -terpinene had a maximum reactivity of 5.3 s^{-1} on 02/08/13 at 2:00 PM LT, which is also when the maximum OH reactivity reported for the whole class of BVOCs occurred. Remarkably, the mean concentration of this compound made it the fourth most abundant BVOC measured, with isoprene being the first (35%), followed by β -pinene (22%), α -pinene (15%), α -terpinene (13%), limonene (9%) and γ -terpinene (1%). The α -terpinene volume mixing ratio was maximum 594 pptv, with an average value between 10:00 AM LT and 5:00 PM LT during the field campaign of 131 ± 110 pptv. Its short lifetime is due to the high reaction rate coefficient towards OH, (as reported in literature, i.e. $3.6\text{ }10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, see Atkinson, (1986) and Lee et al., (2006)), which is more than three-fold higher than the one of reactive isoprene ($k_{\text{isoprene}+\text{OH}}=1\text{ }10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, Atkinson, 1986). Very little is reported in literature regarding its emission rates and ambient levels in the Mediterranean region. Owen et al., (2001) measured α -terpinene from a few Mediterranean tree species, including: *Juniperus phoenicea*, *Juniperus oxycedrus*, *Spartium junceum* L., and *Quercus*

ilex. Ormeno et al., (2007) published the α -terpinene content as 34.9 ± 2.3 $\mu\text{g/gDM}$ in the leaves of *Rosmarinus officinalis*; shrubs of rosemary were present in large quantity around our field site in Corsica.

4.3 Missing reactivity and air masses fingerprint

Figure 2 reports the time series of the total measured OH reactivity and calculated OH reactivity with their associated errors (35% and 20%, respectively). The largest significant discrepancy among those two quantities occurred between 23/07 and 30/07 (an average difference of 56% between measured and calculated OH reactivity). We combined air mass backtrajectories and atmospheric mixing ratios of some common atmospheric tracers to determine the chemical fingerprint of the sampled air and to investigate the origin of the missing reactivity. We chose isoprene and pinenes for air masses influenced by biogenic activity, while propane and CO were used for those enriched in anthropogenic pollutants (see supplement). Maximum concentrations of anthropogenic pollutants were measured when the air masses originated from the North East sector: between 21/07-23/07 and between 31/07-03/08, indicating weak pollution events coming from the industrialized areas of the Po Valley and Milan (Italy). On the other hand, biogenic activity was independent of the wind sector and showed some variability linked to local drivers, such as the air temperature, solar irradiance and wind speed (fig. 6). Remarkably, measured OH reactivity and missing OH reactivity showed no dependency on the origin of air masses.

4.4 Insights into the missing OH reactivity

Here, we consider the contribution of each chemical group to the OH reactivity during the period of the campaign when a significant missing reactivity was observed (July 23rd-30th).

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 monoterpenes 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} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ 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 July 26th when wind speed was lower and increased again after July 27th 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 also temperature dependent. Their emissions are usually fitted to temperature with the expression $E(T) = E(T_s) \exp[\beta(T - T_s)]$, where $E(T_s)$ is the emission rate at T_s , 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, $\beta = 0.11 \text{ K}^{-1}$, 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 $\beta = 0.173 \text{ K}^{-1}$ 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 factors 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. The factor representing sBVOCs 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 significantly 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.

5 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 $5 \pm 4 \text{ s}^{-1}$ (1σ) with a maximum value of $17 \pm 6 \text{ s}^{-1}$ (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, Noelscher et al., 2013, Kumar and Sinha 2014, 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 July 23rd-30th. During this period, the air masses originated from the West (July 23rd-27th and July 29th-30th) and the South (July 27th-29th); calm wind conditions and peaks of air temperature were registered at the field site (28th July). 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 July 23rd-30th we observed increased concentration of BVOCs and OVOCs, lack of pollution events, higher temperature and relatively high missing reactivity ($\sim 10 \text{ s}^{-1}$). 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 July 27th-30th 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 July 27th-30th 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.

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.

Acknowledgements

This study was supported by European Commission's 7th Framework Programmes under Grant Agreement Number 287382 "PIMMS" and 293897 "DEFIVOC"; the programme ChArMEx, PRIMEQUAL CARBOSOR, CEA, CNRS and CAPA-LABEX. We would like to thank the ICOS team from LSCE for the data of CO, Prof. W. Junkermann from KIT/IMK-IFU for kindly lending the Aerolaser instrument and Thierry Leonardis for helping with the gas measurements. Dr. A. Borbon from LISA, Dr. F. Dulac and Dr. E. Hamonou from LSCE are acknowledged for managing the CARBOSOR and ChArMEx projects. We thank the anonymous reviewers for revising the manuscript and Sabina Assan for helping with the English revision.

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Table 1. Measured compounds (whose concentration was above the instrumental detection limits) and their reference group adopted throughout the manuscript for calculating the OH reactivity. AVOCs, BVOCs and OVOCs stand respectively for anthropogenic, biogenic and oxygenated volatile organic compounds.

Species group	Species name
AVOCs	methane, ethane, propane, n-butane, n-pentane, n-hexane, n-octane, n-nonane, n-undecane, n-dodecane, 2-methylpentane, 2-methylhexane, 2,2- dimethylbutane, 2,2-dimethylpropane, 2,3- dimethylpentane, 2,4-dimethylpentane, 2,2,3-trimethylbutane, 2,3,4- trimethylpentane, cyclohexane, ethylene, propylene, 1-butene, 2-methyl-2-butene, 3-methyl-1-butene, 1,3-butadiene, <i>trans</i> -2-butene, <i>cis</i> -2-butene, 1-pentene, <i>trans</i> -2-pentene, <i>cis</i> -2-pentene, hexene, benzene, toluene, ethylbenzene, styrene, m-xylene, o-xylene, p-xylene, acetylene, 1-butyne, acetonitrile.
BVOCs	isoprene, a-pinene, b-pinene, d-limonene, a-terpinene, g-terpinene, camphene.
OVOCs	acetaldehyde, formic acid, acetone, acetic acid, mglyox, methyl ethyl ketone, propionic acid, ethyl vinyl ketone, butiric acid, nopinone, pinonaldehyde, methacrolein, methyl vinyl ketone, formaldehyde, methanol.
Others	NO, NO ₂ , CO.

Table 2. Summary of the experimental methods deployed during the field campaign and needed for calculating the OH reactivity. The number of measured compounds includes the compounds below the instrumental detection limit (LoD).

Technique	Compounds measured	LoD (pptv)
PTR-MS	16 VOCs	7-500
GC- FID/FID	43 NMHCs C2-C12	10-100
GC-FID/MS	16 NMHCs (OVOCs+ C3-C7)	5-100
off-line GC-FID/MS	35 NMHCs C5-C16 + 5 aldehydes C6-C12	5-40

Hantzsch reaction	HCHO	130
CLD	NO _x	50
WS-CRDS	CO ₂ , CH ₄ , CO	1000

Table 3. Relative contributions of individually detected biogenic volatile organic compounds (BVOCs) to the total calculated OH reactivity BVOCs fraction. Daytime BVOCs OH reactivity accounted for a maximum value of 9 s^{-1} , on average it was $2 \pm 2 \text{ s}^{-1}$. Nighttime BVOCs OH reactivity fraction accounted for a maximum value of 0.5 s^{-1} , on average it was 0.1 s^{-1} .

BVOCs	Day (%)	Night (%)
a-pinene	7.7	20.7
b-pinene	16.5	16.1
limonene	12	11.4
camphene	1.5	3.1
a-terpinene	31.1	31.3
g-terpinene	1.3	5
isoprene	30	12.5



Figure 1. Field site top-view, Corsica, France (42.97°N , 9.38°E , altitude 533 m). Measures: 1. PTR-MS, online and offline chromatography for trace gases analysis; 2. OH reactivity; 3. NO_x, O₃,

aerosols composition and black carbon; 4. Meteo, and particles microphysics; 5. HCHO, trace gases and radicals; 6. CO, CO₂, CH₄; 7. Trace gases and particle filters; 8. Particles physics. The photo was shot during the installation of the instruments.

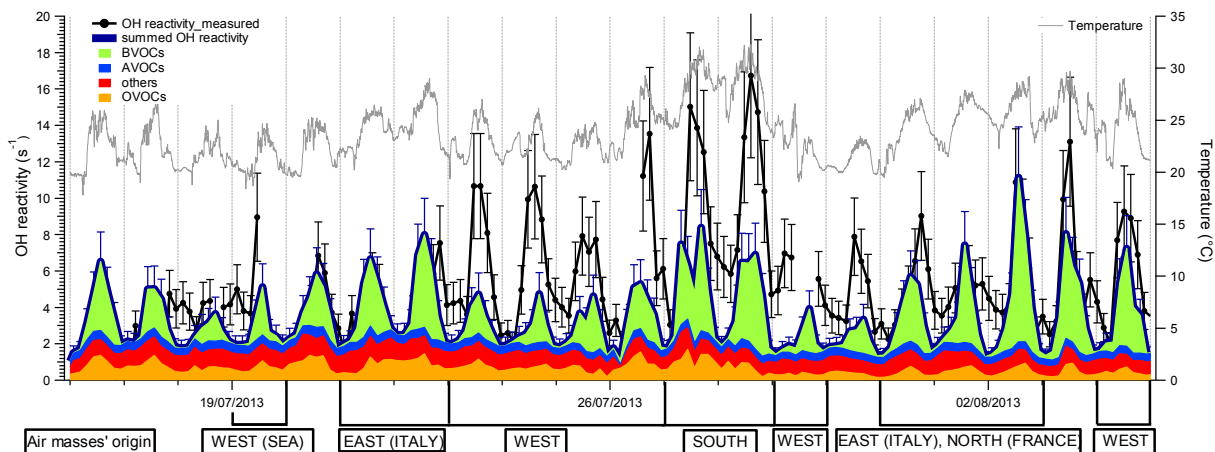


Figure 2. 3-h averaged data of total OH reactivity measured and calculated from the measured gases. Summed OH reactivity is represented with the blue thick line and grouped as biogenic VOCs in green, anthropogenic VOCs in blue, oxygenated VOCs in orange and others in red. Others refer to carbon monoxide (CO) and nitrogen oxides (NO_x).

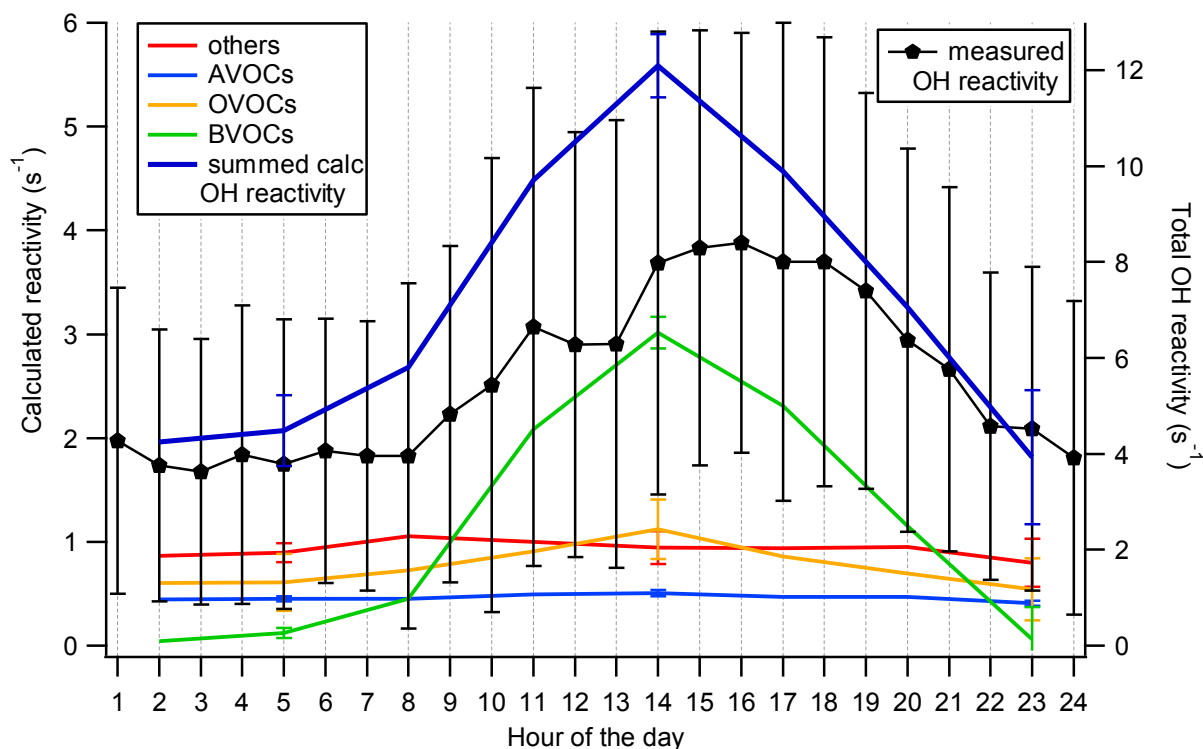


Figure 3. Diurnal patterns of measured (value with $\pm 1\sigma$, right axis) and calculated OH reactivity (left axis). Others, AVOCs, OVOCs, BVOCs are the contribution of CO and NO_x (others), anthropogenic volatiles, oxygenated volatiles and biogenic volatiles to the summed calculated OH reactivity.

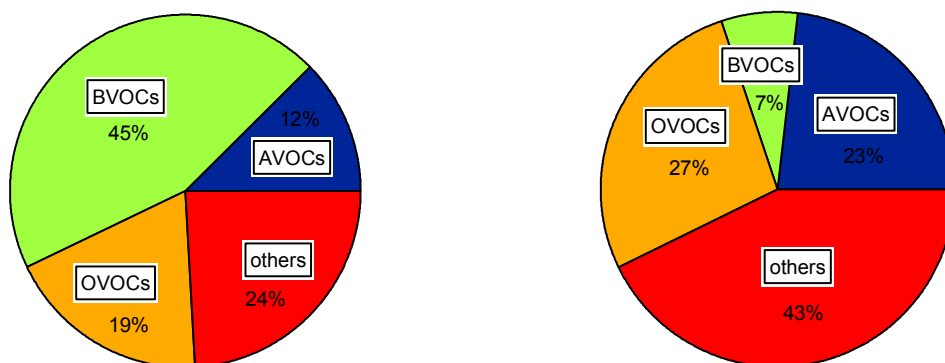


Figure 4. Daytime (left pie) and nighttime (right pie) contributions of the measured compounds to the calculated OH reactivity. Daytime data were collected between 07.30 and 19.30 while nighttime data were between 19.30 and 07.30. Summed OH reactivity during daytime was maximum 11 s^{-1} , on average $4 \pm 2 \text{ s}^{-1}$; while during nighttime it was maximum 3 s^{-1} , on average $2 \pm 0.4 \text{ s}^{-1}$. BVOCs (green), AVOCs (blue), OVOCs (orange) and others (red) stand for biogenic, anthropogenic, oxygenated volatile organic compounds and carbon monoxide and nitrogen oxides, respectively. BVOCs, AVOCs, OVOCs and others contribution was 45%, 12%, 19%, 24%, during daytime; while it was 7%, 23%, 27%, 43% for nighttime reactivity.

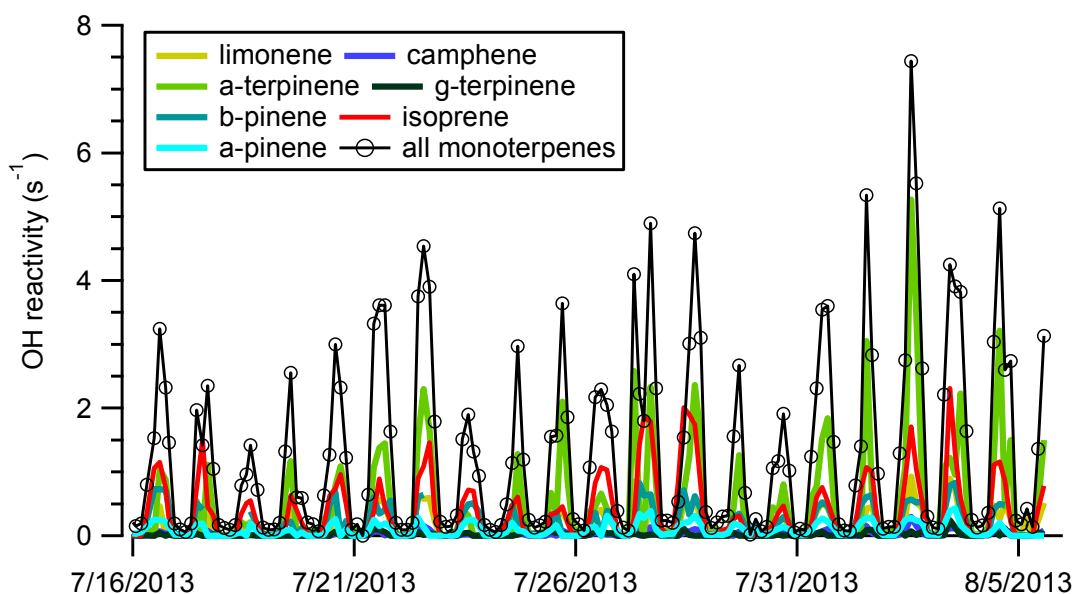


Figure 5. Absolute OH reactivity calculated for the measured biogenic compounds.

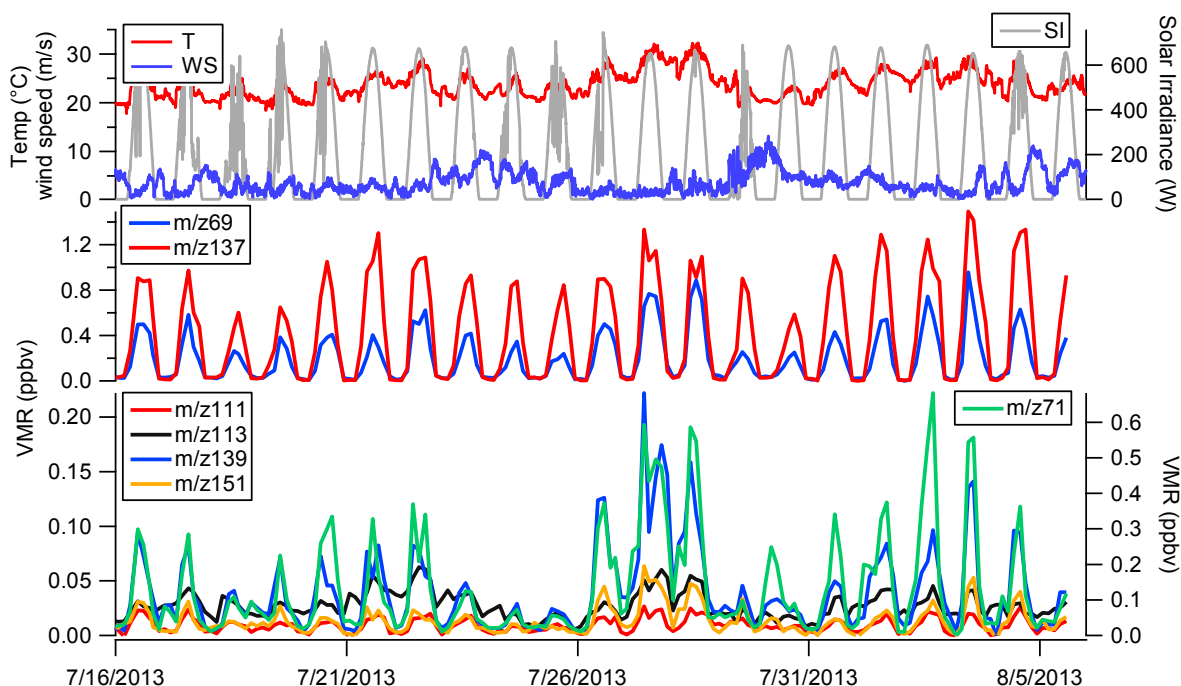


Figure 6. Volume mixing ratios (ppbv) of primary-emitted (mid-panel) and secondary produced biogenic volatile organic compounds (BVOCs) (lower panel) measured by PTR-MS. Primary BVOCs include: isoprene (m/z 69) and monoterpenes (m/z 137), oxidation products include: methyl vinyl ketone, methacrolein, isoprene hydroperoxides MVK+MACR+ISOPOOH (m/z 71), nopinone (m/z 139), pinonaldehyde (m/z 151), m/z 111 and m/z 113. Top panel provides data of temperature, wind speed and solar irradiance.

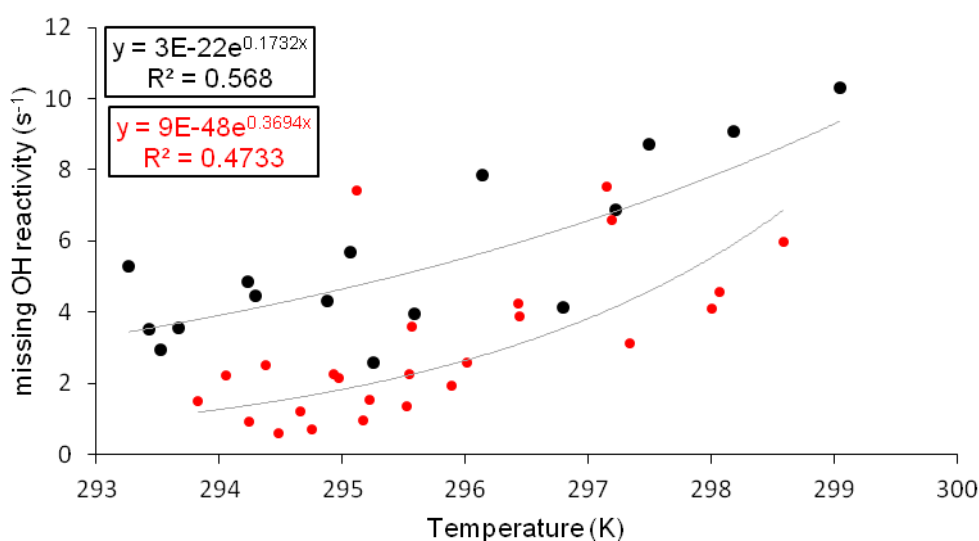


Figure 7. The difference between measured and calculated reactivity (missing OH reactivity) during July 23rd -26th July (red data points) and during July 27th -30th (black data points), dependence to

temperature. The missing reactivity is fitted to $E(T)=E(293) \exp(\beta(T-293))$, with $\beta=0.37 \text{ K}^{-1}$ and $R^2=0.47$ during July 23rd -26th July and $\beta=0.17 \text{ K}^{-1}$ and $R^2=0.57$ during July 27th -30th.

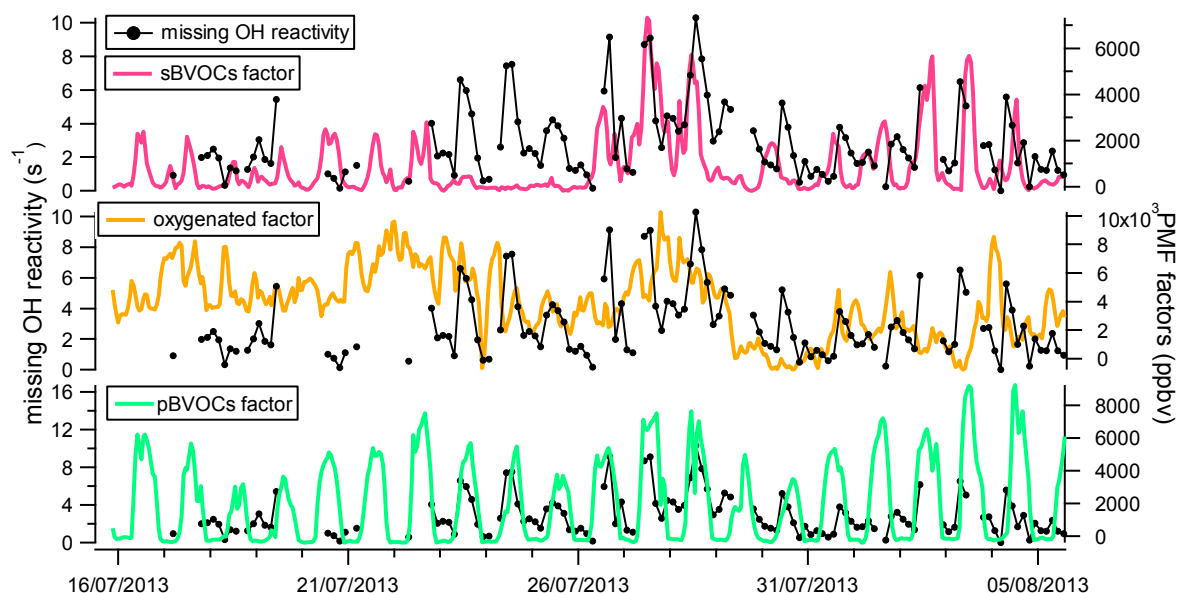


Figure 8. Time series of missing OH reactivity (left axis) reported with the factors obtained from positive matrix factorization analysis (right axis): primary-emitted biogenic volatile organic compounds factor (pBVOCs), oxygenated volatile organic compounds factor and secondary biogenic volatile organic 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.