

Supplement of Atmos. Chem. Phys., 17, 12645–12658, 2017
<https://doi.org/10.5194/acp-17-12645-2017-supplement>
© Author(s) 2017. This work is distributed under
the Creative Commons Attribution 3.0 License.



Supplement of

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

Nora Zannoni et al.

Correspondence to: Nora Zannoni (nora.zannoni@mpic.de) and Valerie Gros (valerie.gros@lsce.ipsl.fr)

The copyright of individual parts of the supplement might differ from the CC BY 3.0 License.

Supplementary material

1. The comparative reactivity method (CRM) instrument

During our campaign we systematically checked the following variables of the CRM instrument: flows (entering and exiting the reactor, sampled flow), pyrrole initial concentration (C1), sensitivity of the PTR-MS towards m/z 68, correction factor for humidity changes between C2 and C3 and correction factor for variations from the assumed pseudo-first order kinetics (summary reported in Table 1). The last type of test was conducted by measuring the reactivity of a known injected test gas (i.e. propane, $k_{\text{propane}+\text{OH}} = (1.1 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, Atkinson et al., (2007)). A correction factor is therefore inferred for the experimental pyrrole/OH regime encountered.

We calibrated the PTR-MS to pyrrole twice during the whole campaign and took an average value from the two calibrations (within 15% difference for the dry calibration factors and within 5% difference for the wet calibration factors). In addition, every time a C1 was measured, we also measured C0 in dry and wet conditions which confirmed the previously determined dry and wet calibration factors.

The C1 value was on average 72 ± 4 ppbv (1σ). The variability was mainly due to flow fluctuations and a systematic reduction of the flow entering the PTR-MS due to clogging of the PTR-MS peek lines with pyrrole. PTR-MS was therefore stopped and cleaned several times during the campaign. For those days where C1 was not measured, an interpolated value was input in eq. (1) (see main text of the manuscript) to determine the measured OH reactivity.

We performed a sensitivity study on the C1 value. For our range of values of measured OH reactivity (from 3 s^{-1} to 22 s^{-1}), C1 changes due to small flow fluctuations (72 ± 4 ppbv) did not affect the final result of reactivity.

We also investigated the sensitivity of the measured OH reactivity to temperature fluctuations inside the container where the CRM instrument was installed ($25\text{-}30^\circ\text{C}$). For the range of measured OH reactivity and recorded temperature values, no significant change in measured reactivity was observed (maximum difference of reactivity of 0.3 s^{-1} for temperature between $25\text{-}30^\circ\text{C}$, see Wallington et al. (1986), for rate coefficients of reactions between pyrrole and OH).

Table S1. Summary of parameters checked and frequency of checks on the CRM instrument

Parameter	Problem	Frequency
Flow	Small fluctuations	Twice a day
C1 value	Flow fluctuations	~ 3 days
Injection of a known reactivity	Correction factor	~ 2 days
PTR-MS flow	Clogging	Twice a day
Cleaning of peek line PTR-MS	Clogging	~ 5 days
Dry and wet calibration m/z 68	PTR-MS sensitivity	Twice all campaign

2. Chemical fingerprint of the sampled air

CO and propane volume mixing ratios were used as tracers for anthropogenic events that reached the site during our field campaign. Peaks of concentrations were observed on 21/07/2016, when air masses coming from East (mainly North of Italy) reached the measuring site.

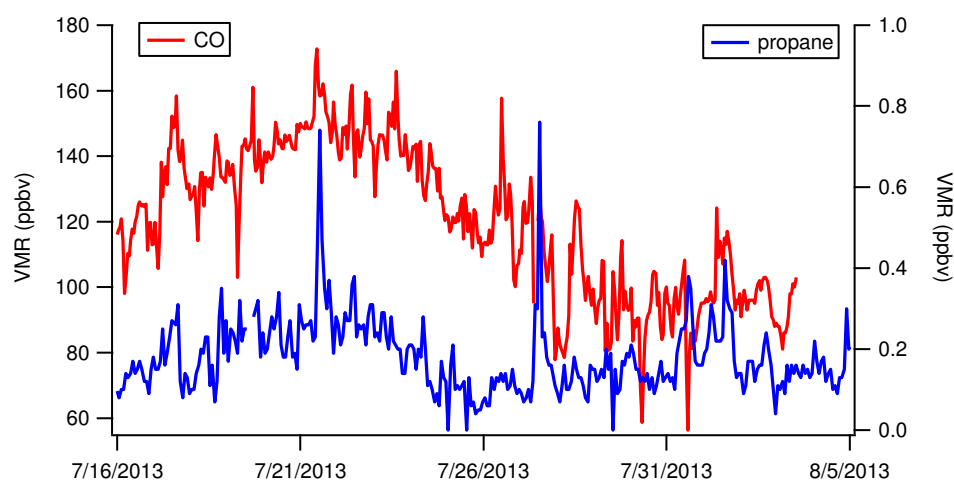


Figure S1. CO and propane volume mixing ratios (ppbv) measured at Cape Corsica during the field campaign.

3. Calculated OH reactivity

The OH reactivity from the measured OH reactants was calculated using the rate constants reported in Table 2 at 298 K.

Table S2. Rate constants for the reactions with OH of the measured OH reactants.

Molecule	k_{i+OH} (cm³molecules⁻¹s⁻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	Vaghjani and Ravishankara, 1991.

4. Missing primary-emitted biogenic volatile organic compounds

Isoprene and monoterpenes concentrations were measured through two different techniques: Proton Transfer Reaction- Mass Spectrometry (PTR-MS) and Gas Chromatography (GC).

Isoprene concentrations correlated for the two techniques but showed systematic higher values for measurements through PTR-MS (see Fig. 2). Such difference can be associated to a systematic interference on m/z 69 measured through PTR-MS, therefore values obtained by GC were used for calculating the OH reactivity.

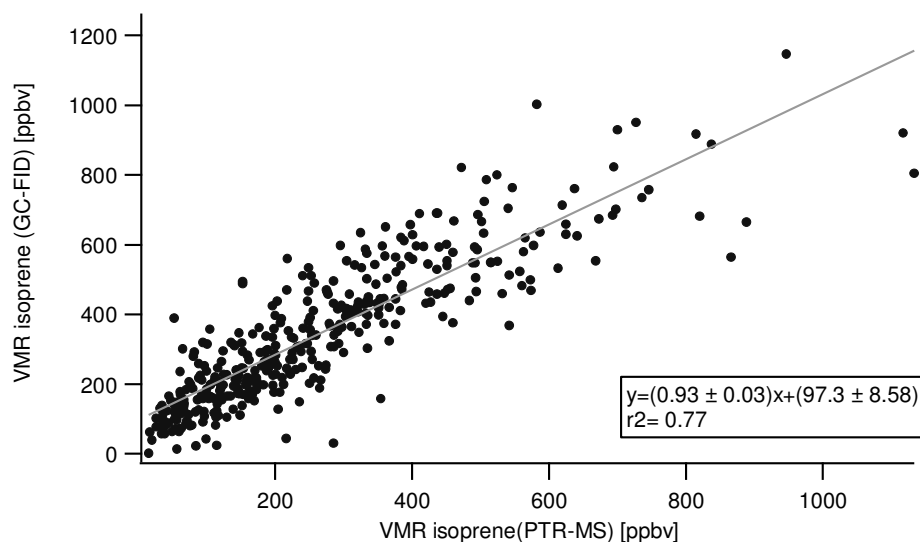


Figure S2. Volume mixing ratio of isoprene measured through GC-FID and PTR-MS (the latter as m/z 69). An overall good correlation is achieved between the two data sets, however, PTR-MS

shows to systematically measure a higher concentration of m/z 69 compared to GC-FID. The data set obtained through GC-FID was retained for calculations of OH reactivity.

The concentration of the total monoterpenes fraction (obtained through PTR-MS) and the summed concentrations of the individually measured monoterpenes (obtained through GC-MS) were compared. Differences between 0.2 and 0.6 ppbv were observed. Such difference corresponds to a value of OH reactivity between 0.8-2.3 s^{-1} , calculated for a weighted rate coefficient of reaction towards OH of the emission pattern of a Mediterranean shrub species present in the surrounding of the field site (see main text). Figure 3 shows the two concentrations compared. Such missing OH reactivity is distributed along the whole time of sampling at the site.

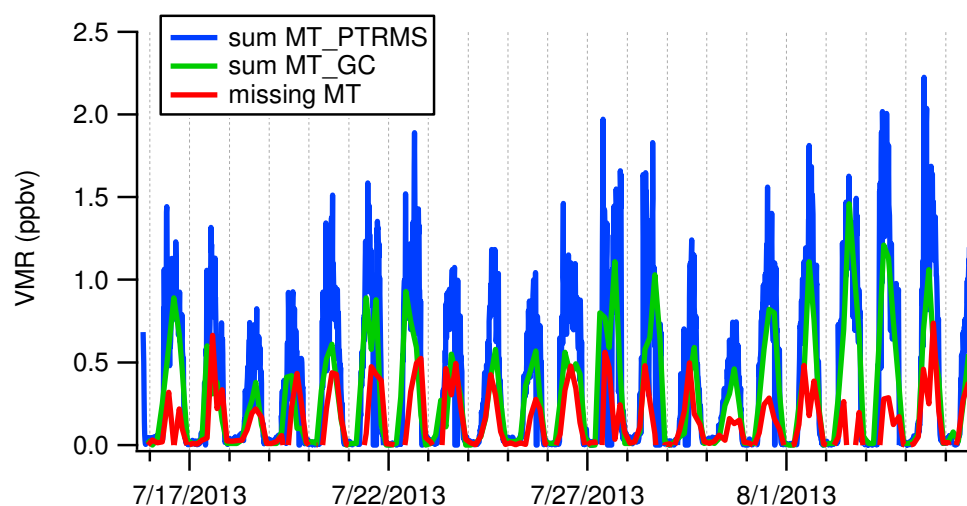


Figure S3. Difference in concentration among the measured total monoterpenes fraction by PTR-MS (blue) and the summed individually measured monoterpenes by GC (green). The unmeasured monoterpenes concentration is reported in red.

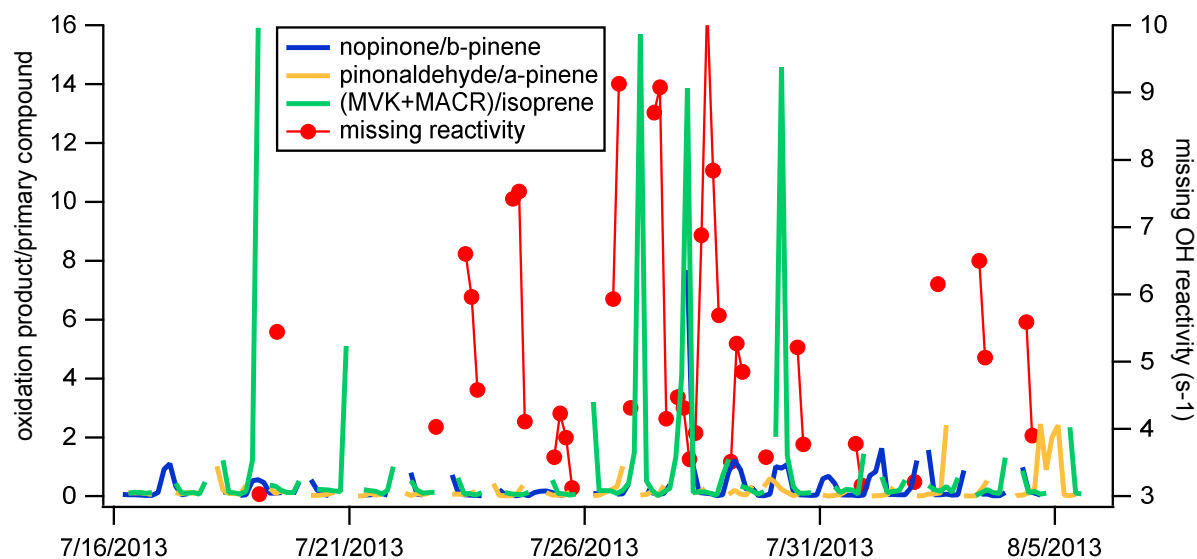


Figure S4. Missing OH reactivity and ratio between oxidation product and primary compound for some biogenic molecules (nopinone/ β -pinene in blue, (MVK+MACR)/isoprene in green, pinonaldehyde/ α -pinene in yellow and the missing reactivity is in red).

References:

Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions, *Chem. Rev. - CHEM REV*, 86(1), 69–201, doi:10.1021/cr00071a004, 1986.

Atkinson, R., Baulch, D. L., Cox, R. A., Jr, R. F. H., Kerr, J. A., Rossi, M. J. and Troe, J.: Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement VI. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, *J. Phys. Chem. Ref. Data*, 26(6), 1329–1499, doi:10.1063/1.556010, 1997.

Atkinson, R.; Baulch, D.L.; Cox, R.A.; Crowley, J.N.; Hampson, R.F, Jr.; Kerr, J.A.; Rossi, M.J.; Troe, J.: Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry Web Version December 2001, pages 1 – 56, 2001.

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmos. Environ.*, 37, 197–219, doi:10.1016/S1352-2310(03)00391-1, 2003.

Atkinson, R. and Aschmann, S.M.: Atmospheric chemistry of the monoterpene reaction products nopinone, camphenilone, and 4-acetyl-1-methylcyclohexene, *J. Atmos. Chem.*, 16, 337 – 348, 1993.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I - gas phase reactions of Ox, HOx, NOx and SOx species, *Atmos Chem Phys*, 4(6), 1461–1738, doi:10.5194/acp-4-1461-2004, 2004.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J. and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – gas phase reactions of inorganic halogens, *Atmos Chem Phys*, 7(4), 981–1191, doi:10.5194/acp-7-981-2007, 2007.

Baulch, D.L.; Bowers, D.G.; Malcolm, D.G.; Tuckersman, R.T.: Evaluated kinetic data for high-temperature reactions. Volume 5. Part 1. Homogeneous gas phase reactions of the hydroxyl radical with alkanes, *J. Phys. Chem. Ref. Data*, 15, 1986.

Boodaghians, R.B.; Hall, I.W.; Toby, F.S.; Wayne, R.P.: Absolute determinations of the kinetics and temperature dependences of the reactions of OH with a series of alkynes, *J. Chem. Soc. Faraday Trans. 2*, 83, 1987.

Chiorboli, C., Bignozzi, C.A., Maldotti A., Giardini P.F., Rossi A., and Carassiti V.: Rate constants for the gas-phase reactions of OH radicals with b-dimethylstyrene and acetone. Mechanism of b-dimethylstyrene NOx-air photooxidation, *Int. J. Chem. Kinet.*, 15, 579-586, 1983.

Davis ME, Talukdar RK, Notte G, Ellison GB, Burkholder JB.: Rate coefficients for the OH + pinonaldehyde (C₁₀H₁₆O₂) reaction between 297 and 374 K, *Environ Sci Technol.*;41(11):3959-65, 2007.

Dillon, T. J. and Holscher, D. and Sivakumaran, V. and Horowitz, A. and Crowley, J. N.: Kinetics of the reactions of HO with methanol (210-351 K) and with ethanol (216-368 K), *Phys. Chem.*, 7, 349-355, 2005.

Grosjean, D. and Williams, E.L., II: Environmental persistence of organic compounds estimated from structure-reactivity and linear free-energy relationships. Unsaturated aliphatics, *Atmos. Environ. Part A*, 26, 1395 – 1405, 1992.

McGillen, M.R.; Percival, C.J.; Shallcross, D.E.; Harvey, J.N.: Is hydrogen abstraction an important pathway in the reaction of alkenes with the OH radical?, *Phys. Chem. Chem. Phys.*, 9, 4349 – 4356, 2007.

Raff JD, Stevens PS, Hites RA.: Relative rate and product studies of the OH-acetone reaction, *J Phys Chem A*, 109(21):4728-35, 2005.

Sprengnether, M.M.; Demerjian, K.L.; Dransfield, T.J.; Clarke, J.S.; Anderson, J.G.; Donahue, N.M., Rate Constants of Nine C6-C9 Alkanes with OH from 230 to 379 K: Chemical Tracers for [OH], *J. Phys. Chem. A*, 113, 5030 – 5038, 2009.

Vaghjiani G. and Ravishankara A.R.: New measurement of the rate coefficient for the reaction of OH with methane, *Nature* 350, 406 – 409, doi:10.1038/350406a0, 1991.

Wallington, T. J.: Kinetics of the gas phase reaction of OH radicals with pyrrole and thiophene, *Int. J. Chem. Kinet.*, 18(4), 487–496, doi:10.1002/kin.550180407, 1986.

Wilson, E.W.; Hamilton, W.A.; Kennington, H.R.; Evans, B.; Scott, N.W.; DeMore, W.B., Measurement and estimation of rate constants for the reactions of hydroxyl radical with several alkanes and cycloalkanes, *J. Phys. Chem. A*, 110, 3593 – 3604, 2006.

Zetzsch, C. and Stuhl, F.: Rate constants for reactions of OH with carbonic acids, *Phys. Chem. Behav. Atmos. Pollut. Proc. Eur. Symp.*, 1982.

Zhu, L.; Talukdar, R.K.; Burkholder, J.B.; Ravishanker, A.R.: Rate coefficients for the OH plus acetaldehyde (CH₃CHO) reaction between 204 and 373 K, *Int. J. Chem. Kinet.*, 40, 635 – 646, 2008.