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, $k_{propane+OH}= (1.1\pm0.2)\times10^{-12}$ cm^3 molecule^{-1} 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). Such variability was mainly given by flows fluctuations, including 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 flows 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 (25-30°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 25-30°C, see Wallington et al., 1986 for rate coefficients of reactions between pyrrole and OH).

Table 1. Summary of parameters checked and frequency of checks on the CRM instrument

Parameter	Problem	Frequency
Flows	Small fluctuations	Twice a day
C1 value	Flows 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.
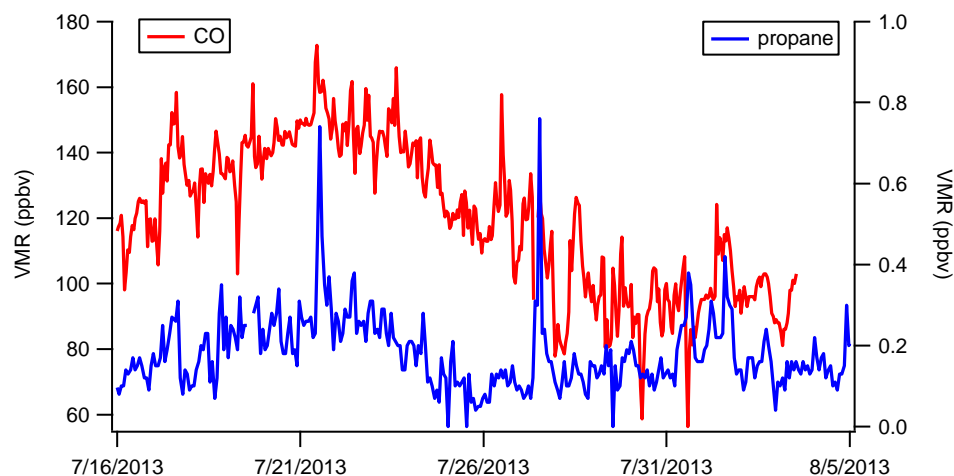
Figure 1. CO and propane volume mixing ratios (ppbv) measured at Cape Corsica during the field campaign.

3. Missing monoterpenes

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

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 2 shows the two concentrations compared. Such missing OH reactivity is distributed along the whole time of sampling at the site.
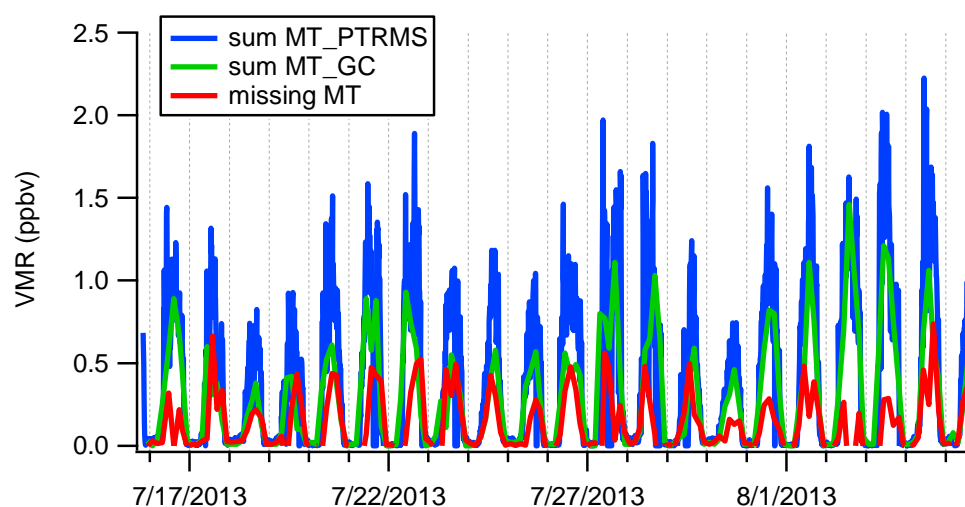
Figure 3. Difference in concentration among the measured total monoterpenes fraction by PTR-MS and the summed individually measured monoterpenes by GC.

References:

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.

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.