***Comparison of OH and OH reactivity,* COMPOH**

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- **Introduction and motivation**

A large number of chemical species with diverse structures are emitted into the atmosphere from biogenic and anthropogenic sources. Each can be oxidized by OH, O3 and NO3 to a multitude of further products resulting in a complex cocktail of volatile organic compounds. In 2001 a new measurement technique called "OH reactivity" was devised by Kovacs and Brune in 2001. This pioneering study showed that by adapting a Laser Induced Flouresence (LIF) technique for measuring OH with a flow tube it was possible to determine the total sink for OH in the atmosphere directly rather than measuring all relevant species individually. Three alternative measurement systems for OH reactivity have been subsequently developed: a flow tube-LIF combination (e.g. Kovacs and Brune 2001), a pump and probe-LIF method (e.g. Sadanaga et al. 2004, Parker et al. 2011), and a comparative reactivity measurement (CRM) initially based on proton transfer reaction mass spectrometry (Sinha et al. 2008). A comparison of these different techniques has not yet been made. In this OH and OH reactivity campaign "COMPOH" campaign, the opportunity was taken to compare: two different CRM techniques with PTR-MS; a new CRM technique with GC-PID; and the LIF system.

The COMPOH campaign took place at the SIRTA measurement site from June 20th until July 13th. Within the framework of this intercomparison the Max Planck Institute undertook OH reactivity measurements using the CRM method both with the standard PTR-MS type measurement and with a new GC-PID system. These were compared with another CRM technique with using ambient measurements and a series of interferences tests, most notably NO.

- **Scientific objectives**

The science objectives for this campaign were 1) to compare OH reactivity measurements made with different techniques, and 2) to provide OH reactivity measurements during an intercomparison of OH measurement techniques namely CIMS and LIF.

- **Reason for choosing station**

The SIRTA station was chosen for several reasons. The site is impacted by rural continental air (for background reactivity values) and occasionally by the pollution plume of Paris which lies ca. 20km to the northeast of the site. In this way a span of OH reactivities and pollution levels, conducive to comparison, can be expected during the campaign. Furthermore meteorological and OH CIMS instrumentation were already at the site.

- **Method and experimental set-up**

In the CRM method for measuring OH reactivity, a reactive molecule (X), not normally present in air, is passed through a glass reactor and its concentration is monitored at ppbv levels with a suitable detector. OH radicals are then introduced in the glass reactor at a constant rate to react with X, first in the presence of zero air and then in the presence of ambient air containing VOCs and other OH reactive species. Comparing the amount of X exiting the reactor with and without the ambient air allows the OH reactivity in ambient to be determined. In the first version of this set up, molecule X was pyrrole (C5H4N) and the detector used was a proton transfer reaction

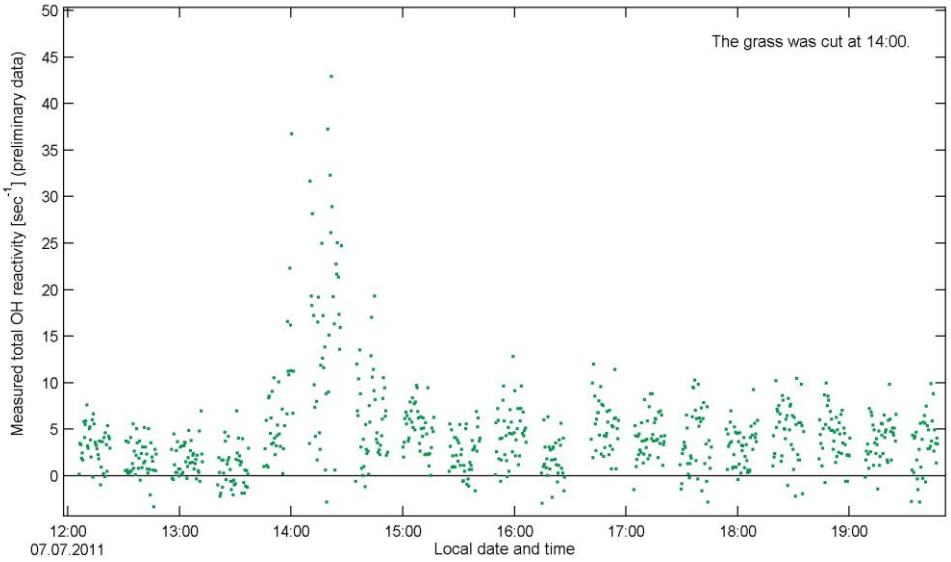
spectrometer (PTR-MS), although in principle any detector may be used if a suitable molecule is available. The PTR-MS has been used extensively over the last decade to measure ambient VOCs (Lindinger et al. 1998). If a molecule of interest has a proton affinity greater than water and is at sufficient concentration it may be measured by PTR-MS. An advantage of the CRM method is that it requires only the precise quantification of a stable VOC at ppbv levels rather than the more technically challenging LIF based measurement of highly reactive OH radicals at concentrations more than 103 times lower.

- **Preliminary results and conclusions**

1) Side by side comparisons of two CRM systems were made for the first time. These systems were configured slightly differently, and this campaign should permit an assessment of the two different regimes.
2) The MPI OH reactivity systems (both GC-PID and PTR-MS) and measured ambient air the remote continental site throughout the campaign with minimal instrumental problems. As well as in relatively clean ambient conditions when the air came from the south or southwest (reactivity ca.5 s-1), measurements were also made in the Paris plume which was advected over the site in the period 3rd-5th July.
3) The Paris plume impacted the site at the time that CIMS and FAGE techniques for the measurement of OH were being compared. Thus we have obtained in-situ OH, the OH sink (OH reactivity) and measurements of several key sources (ozone, CH2O, HONO).
4) The impact of high NO concentrations on the OH reactivity measurement was examined both in ambient data situations (when NO increased to ca. 15 ppbv) and in careful sequential additions of NO from a standard). This is the most thorough examination of this interference done to date.
5) On the 7th of July we arranged that grass surrounding the measurement station would be cut with a motorized lawn mower. This released significant quantities of biogenic “wounding” compounds such as hexenol and hexenal from the grass and significant quantities of NO from the lawnmower motor. This enabled the NO sensitivitites to be examined in ambient mixtures of VOC. Figure 1a shows the lawnmower in operation at the site, and Figure 1b the peak in reactivity observed in the raw data.

Figure 1a

Figure 1b



6) In the final stages of the experiment the CRM OH reactivity set-up and the FAGE OH reactivity were measured in parallel, providing for the first time a dataset with which the two techniques may be compared.

- **Outcome and future studies**
  The data from all instruments must first be worked up and corrected for known interferences before final conclusions can be drawn. However, data for this comparison has been successfully obtained and a workshop has been planned in November for the detailed discussion of the results. The experience from this study can be taken forward into future intercomparisons.

- **References**

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