Atmospheric Measurement Techniques Discussions

Interactive comment on "A new method for total OH reactivity measurements using a fast Gas Chromatographic Photo-Ionization Detector (GC-PID)" *by* A. C. Nölscher et al.

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Many thanks for the encouraging and helpful comments of referee 2. As already stated by the first reviewer, the title of the presented manuscript should be changed to: "Total OH reactivity measurements using a new fast Gas Chromatographic Photo-Ionization Detector (GC-PID)".

According to the referee comments, more quantification would be valuable particularly for potential interferences and effects of relative humidity. We will provide the supplementary information requested by the reviewer. Detailed answers for the specific

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comments are given below:

2.1) A more detailed description of how hysteresis, changing sensitivity, humidity changes, and NO are accounted for in the reactivity calculation would be informative.

The referee refers to Section 2.1 (p.3580, ls.15-20). In this paragraph a list of potential correction terms is given, that have to be taken into account for total OH reactivity measurements using CRM. 1) Hysteresis occurs for example, when valves are switched, detectors are not exactly synchronized (inducing transitory changes in signal of typically 0.5 - 10 seconds duration), or when the UV lamp is initially switched on (at least half an hour for warming up). Data points affected by these effects simply have been deleted and were excluded from any analysis. 2) Sensitivity changes in general complicate the measurements. Rapid jumps need to be excluded, while slowly decreasing sensitivity must be accounted for by calibrations. 3) To correct for different humidity levels in C2 and C3, a humidity-response-calibration was done. For this, different water levels were applied to the measurement of C2, which resulted in variations of OH production. This calibration was used to correct parts of the data, where baseline (C2) and measurements (C3) were consistently showing different humidity levels. Sharp peaks in ambient humidity and rapid changes were filtered from the data-set. 4) A correction to account for deviations for pseudo first order conditions is necessary using CRM as was already described by Sinha et al 2008, ACP. Since the presented measurements usually contained a mixture of pyrrole/OH about 1.7-3.0 (Section 2.1, p.3580, l. 14) a small correction (ca. 8%) was calculated and applied. 4) NO was always measured alongside and never reached levels, that could cause an interference in the CRM system (see Nölscher et al 2012a, ACPD). All studies conducted with the presented set-up were deployed in natural, biogenically influenced environments with relatively little NO. A detailed discussion of a similar set-up used for highly polluted environments is given in Dolgorouky et al 2012, ACPD. 5) Flows inside the CRM system are regularly checked and monitored. Thus a dilution factor for ambient air probes due to the addition of nitrogen and pyrrole is easily obtained. Typically, the analyzed mixture contained 70 %

ambient air and 30 % nitrogen and pyrrole (Section 2.4 p. 3586, l.12).

2.2) The system is described as a custom built GC-PID system from Environics-IUT GmbH. How is this system different from those commercially available?

Close cooperation between Environics-IUT GmbH and our group at MPI-C allowed optimization of the original system for pyrrole detection. Sensitivity was improved, interferences were minimized, and the separation of water and pyrrole peaks was modified. The modified version of this instrument (optimized for pyrrole) is available for purchase from the company.

2.3) In Figure 1, why use arbitrary units for time and counts for signal instead of seconds and concentration? What is the cause for the offset observed? Why is the H_2O signal inverted?

Figure 1 displays a typical chromatogram delivered by the instrument as raw signal. That is why counts and arbitrary units were used. Time is measured as 2048 equal steps in the time set for one analysis, e.g. 60-70 s. For each time-step ions are counted after the sample left the column and has been ionized by UV. Hence, the signal drawn here needs to be analyzed, integrated in terms of peak area, and compared to a calibration in order to convert the peak area to a mixing ratio. (An additional axis with seconds will be added to the plot for clarity.)

The offset results from a mixture of various effects: 1) Traces of ionizable compounds e.g. from out-gassing material are detected in addition to the analyzed sample. 2) Photo effect on the collector directly induced by UV radiation. 3) Electrical noise of the multiplier increases the offset.

Water, as it also absorbs in the UV, takes up energy as soon as it leaves the column and enters the detector. This energy, which usually causes the background, is now no longer available for ionization. Hence, the signal drops and we observe an "inverted peak". This will be added to the revised version of the paper.

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2.4) In the standard tests performed with propane and propene, give a quantified value of how the rate coefficients or rates measured compare with the published values. What does "generated reasonable and comparable results" mean?

Many thanks for this comment. In Figure 7 the response of both detectors is compared, and they show very good agreement. The given correlation coefficient (Pearson R) is with R=0.97 close to 1. Whether each of the detectors responded accurately in terms of total OH reactivity measurements for the two tested compounds is not visible in this Figure. Therefore, the paragraph will be modified and more details included. Compared to the theoretically expected total OH reactivity from the standards, the PTR-MS measurements reached 97 % and the GC-PID values 92 %. Both instruments slightly underestimated the true total OH reactivity (as compared to the stated values on the calibration bottle) by less than 10 % in the presented tests. Hence, in terms of total OH reactivity both detectors responded accurately and within the uncertainty when used for CRM measurements.

2.5) In Figure 8, it appears that values are plotted that are below the stated LOD – even a couple of negative values. Perhaps it would be good to put a shaded area showing the LOD and below, or to remove those points altogether as they have no statistical meaning. A few more sentences detailing the Diel behavior of the reactivity and why it rose to 40 s-1 would be informative.

Indeed, some points scatter in the limit of detection. We agree with the referee that an indication of the LOD as grey shaded area can be useful and the graph will be modified. We will further describe the diel variations in the OH reactivity as requested. Figure 8 shows two days of the HUMPPA-COPEC campaign 2010, which was conducted in the summertime within the Finnish boreal forest. Diel variation is weak for the 7th of August, which was characterized by strong mixing and rain in the afternoon. Total OH reactivity reached highest values shortly after a storm, as the boundary layer height started to decrease. A stronger signal for total OH reactivity was found the following day when maximum values of around 40 s-1 were reached in the late afternoon. As

the day before, this day was stormy but warmer in temperature. Between strong rain showers high boreal forest emissions due to irradiation and high temperatures (which drive the VOC emissions) are likely causing the measured total OH reactivity to be high.

2.6) In Figure 10, the data for Sep 10 – Sep 11 before 12:00 PM there appears to be an offset between the GC-PID and the PTR-MS values. Then there is a break in the data after which the GC-PID data becomes noisier, but with better overlap. What changed? Again values below the stated LOD are plotted. How hard is it to clean/service the detector?

Comparison of Figure 10 and 11 leads to the conclusion that the noise of the GC-PID in the conditions for the Jülich plant chamber measurements is too strong to adequately measure such low total OH reactivity levels. The correlation between the two instruments is very bad and many measurement points are obtained below the limit of detection. It seems that the GC-PID monitored slightly higher values on September 11 before 12:00 PM. Due to a software problem the PTR-MS data was not saved from midnight onwards. The instrument kept running and no instrumental settings were changed.

Maintenance of GC-PID detector was provided by the company Environics-IUT Berlin. The cooperation was good and according to the required needs and time-frames (e.g. for campaigns) reliable service was provided. Nevertheless shipment delays are inconvenient for field usage, and future device designs will make the access of PID window and particle filter easier for the user.

2.7) The "Discussion and comparison" section is really a summary – perhaps change the section title.

Okay, this will be done.

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