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Biogeosciences Discussions

Interactive comment on "Seasonal measurements of total OH reactivity fluxes, total ozone loss rates and missing emissions from Norway spruce in 2011" *by* A.C. Nölscher et al.

A.C. Nölscher et al.

a.noelscher@mpic.de

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The referee is thanked for recognizing the novelty of this study and for the detailed remarks concerning several important issues of the manuscript. The comments will be answered in the following text and changes will be applied to a revised version of the manuscript.

First general comment: We agree with the reviewer that the terminology must be kept consistent in order to avoid confusion. For this reason we now adopt TOHRE throughout the revised manuscript and have altered the title to "Seasonal measurements of total OH reactivity emission rates from Norway spruce in 2011".

1. How often was the VOC-PTR-MS calibration performed? Or was the concentration derived from PTR-MS compared with the concentration from GC-MS results for each season? The differences between measured and calculated TOHRE are quite different in different seasons (small difference at first but large difference at last). I just worried if the results of the VOC-PTR-MS were calibrated only at first, so that the concentrations became underestimated later in the measurement period.

The PTR-MS for measuring VOCs was calibrated at the measurement site regularly throughout the year. Calibrations of interests for the presented results were performed on 10.May, 07.July, and 11.Nov 2011. Calibration factors for all monitored compounds were found to be relative stable over the entire measurement period. They varied by less than 10% (e.g. for the signal of total monoterpenes: k= 1.8-2.2x10-9 molecules cm3 s-1).We will clarify this in the description of the VOC-PTR-MS in the manuscript.

2. Page 13505 line 15: During cuvette closure, is there any decrease of trace species (NO2, CO. . .) like O3? If the uptake of trace species is important, the observed TOHRE will be underestimated. For example if NO2 is absorbed to the surface of the cuvette or uptaken by the plant, observed total OH reactivity would decrease and the slope for TOHRE calculation would decrease as well. And if the absorption of NO2 happens and it has humidity dependence, this would cause seasonal differences.

According to the referee's comment an uptake of e.g. NO2 to the cuvette surface could cause a concentration decrease which might depend on temperature and humidity, hence has a seasonal effect in causing an underestimation of the directly measured TOHRE. Indeed, this is an insightful comment. Unfortunately NO2 as well as CO were not detected inside the cuvette enclosure. Therefore, we cannot estimate the impact of this possible effect on our measurements.

Nevertheless, during the intensive field measurement campaign on top of Kleiner Feldberg (PARADE) in August/September 2011 ambient levels of NO2 and CO were monitored some 100 m from the cuvette location. In terms of OH reactivity contributions,

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these were detected to be on average 0.6 s-1 for NO2 (corresponding to ambient concentration levels of ca. 2ppb) and 0.36 s-1 for CO (103 ppbV).

Recent findings (Breuninger et al 2012, 2013) demonstrate a substantial uptake of NO2 by spruce. Transferring these interpretations to our cuvette, we may estimate a 30% decrease of NO2 within the closed system.

However, compared to the relatively high values of total OH reactivity that were found for most of the time inside the closed cuvette due to the primary emissions (10-300 s-1), these values are small and possible decay of ambient trace species inside the cuvette during closure does not likely impact significantly the measurements of emission rates.

As the manuscript shows, the main contributors to the total OH reactivity in the cuvette are the monoterpenes. These non-polar species are not very soluble and thus unlikely to be significantly affected by humidity modulated uptake. A very soluble species is methanol. If uptake to cuvette surfaces would be triggered by humidity, anti-correlation of methanol and water measurements should be visible. No such dependency was observed when applying the correlation. Also, during closures methanol increases linearly independent of ambient humidity in similar fashion to the total monoterpene signal. In the revised manuscript a discussion of this interesting remark will be added.

3. Page13505 line18: Why data point of total OH reactivity measurements change? I imagine you can control the measurement time period.

Yes, the cuvette control was set to close the system in a 20 minute cycle for 3 minutes. This control was not synchronized with the CRM control. By using the Comparative Reactivity Method the measurements alternate between sampling and reference periods. During the reference periods, the concentration level of a reagent with OH alone is monitored by the detector (PTR-MS). At that times, the instrument draws air through a catalytic converter instead of sampling directly from the cuvette enclosure. Due to the non synchronized controls of both cycles (cuvette opening/closing and the CRM switching) occasionally the number of data points during closures was reduced. As

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already described in the manuscript, if the number of data points was less than 8 the closure was excluded.

4. Page13506 line 20: Wall loss is assumed to be constant. But I am afraid it is dependent on relative humidity or other factors.

The deposition of ozone to the cuvette walls was characterized by an empty chamber experiment. It was found to be constant and of minor importance with a maximum loss of 6 pptV/s . This important detail will be added to a new version of the manuscript.

5. Page13508 line13, page13516 line17: Is it possible to estimate roughly the ratio of uncalibrated and unidentified peaks to measured terpenes? If they are only minor, it is no matter. But if they are major, it would be important as explanation for discrepancy of THORE during late seasons.

Indeed, unidentified and uncalibrated peaks in the GC-MS analysis could be of interest to the discussion concerning unexplained TOHRE. It is known, that many compounds are released by the biosphere, which are surely not captured via the PTR-MS measurements (e.g. ethane). Some of these are potentially important to explain the high discrepancy. The GC-MS measurements were conducted in single ion mode (SIM). Thus the scope for measuring and indeed identifying additional compounds was limited. Nevertheless, some additional peaks were detected albeit not an entire spectrum was monitored. But since these peaks are representing unidentified and uncalibrated compounds, from our experimental data, we have no means to estimate their contribution to the total OH loss rate.

6. Page13512 (Fig.8): With TOHRE, different factors are shown in right side for each period (b – e). I just wonder how these factors changes during other seasons? Strong wind makes high TOHRE? Unexpected TOHRE was observed with high benzene (m/z=79)? Total O3 loss rate are similar variation of TOHRE? Methanol is decreased during night during other seasons?

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Figure 8 shows examples of the data for each period. For each Figure the most striking example was chosen, in order to point out the different impacts on TOHRE throughout the season. Instead of adding more graphs, in order to present the behavior of these factors with changing seasons, a table with correlation coefficients will be included into the manuscript (see attached Figure 1). Here the Pearson R coefficients between various factors and TOHRE for all defined periods are summarized.

The Pearson correlation coefficient close to one shows good correlation for calculated and measured TOHRE in springtime. At that time almost the entire OH loss rate inside the cuvette could be explained by the PTR-MS detected sink compounds. In spring, also temperature and the total monoterpene emission rate correlated well with the measured TOHRE. In summer TOHRE was in good agreement with most of the tree emissions, including benzene, which has a low Pearson R for all the other defined periods. Only in autumn, ambient ozone levels correlated to TOHRE.

7. Page13513 line13: It is very surprising benzene was high when missing TOHRE was high. Is benzene checked by GC-MS? Or It is just m/z= 79 detected by PTR-MS? Is it possible that some unknown biogenic species make fragmentation peak at m/z=79 in PTR-MS?

For most times the benzene signal detected by the PTR-MS was very low. Only for local pollution (e.g. car exhaust) it increased and the data was filtered and removed for these occasions. One event remained with unusually high benzene emission rates, that were observed on the 9th of June. Lateron it was found that the branch was damaged most probably during the windy days prior to this date. For the high temperature during this day, both total OH reactivity and benzene emission rates increased significantly. It has already been found in previous studies (Heiden et al., 1999, White et al., 2009, Dudareva et al., 2006) that benzenoid emissions from plants might occur during stress conditions. Also, past studies (e.g. de Gouw and Warneke 2006) which have connected a GC separation column ahead on the PTR-MS have shown no (or for the atmosphere irrelevant) interfering compounds on m/z 79. For clarity, one sentence will

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be added here.

8. Table2 : About the values of ambient O3. Are they average of maximum concentration? If this is average of entire period (include daytime, night time), standard deviation seems be too small.

It is an average for the entire periods, using the standard error as uncertainty. The standard error is defined as standard deviation over the square root of the number of data points. We will make this point clearer in the manuscript by rewording to define the standard error in the text. The proposed technical corrections will be taken into account in the revised version of the manuscript.

Interactive comment on Biogeosciences Discuss., 9, 13497, 2012.

	Spring	Early summer	Late summer	Autumn
Temperature (ambient)	0.447	0.176	0.440	0.402
Ozone (ambient)	0.350	0.152	0.292	**0.513**
Relative humidity (ambient)	-0.293	-0.193	-0.283	-0.335
Water (ambient)	0.211	0.007	0.228	0.113
NO (ambient)	0.091	0.010	0.032	0.137
NO2 (ambient)	-0.007	0.164	0.031	0.229
Global radiation	0.353	0.169	0.389	0.142
Temperature (cuvette)	**0.517**	**0.519**	0.494	0.409
Ozone (cuvette)	0.337	0.186	0.177	0.265
Relative humidity (cuvette)	-0.327	-0.388	-0.305	-0.340
Methanol	0.201	0.406	0.309	0.325
Acetaldehyde	0.265	**0.588**	**0.533**	0.215
Acetone	0.327	**0.693**	**0.561**	0.312
Isoprene	0.268	**0.651**	**0.557**	0.315
Benzene	0.259	**0.680**	0.131	0.187
Ethanol	0.274	**0.541**	0.438	0.198
Linalool	0.250	0.182	0.060	0.207
Pinonaldehyde	0.125	0.061	0.051	0.205
Total nopinone	0.274	**0.541**	0.438	0.198
Total monoterpenes	0.492	**0.534**	0.448	0.190
Total sesquiterpenes	0.358	0.363	0.398	0.450
TOHRE (calculated)	**0.842**	**0.590**	0.493	0.251
TOHRE (model)	**0.569**	**0.575**	**0.575**	0.398

Fig. 1. Pearson correlation coefficients calculated for measured TOHRE and various parameters.

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