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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.

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The referee is thanked for the critical review and discussion of the submitted manuscript. We were very pleased that the reviewer also noted the uniqueness of the work and termed it a timely contribution. In the following, we will discuss in detail the questions raised and include the amendments into a new version of the manuscript.

1) While I value the intent of this research and some of its results, I see fundamental problems with the description and execution of the experiment and a multitude of areas where the presentation in the manuscript does not meet expected BG standards. I find the organization of the manuscript unfortunate. A more succinct presentation showing

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how the primary findings are supported by the data would be preferable over the current rather lengthy and at times redundant discussion of the seasonal data details.

The referee generally criticizes the overall presentation of the manuscript without giving any specific details. We will endeavor to make the current text more succinct and remove any redundancy.

E.g. Figure 4 and 5 will be rearranged (as suggested by Referee2), an additional Figure (please find it attached to this answer: Figure 1) will be included to shorten some text, the discussion section will be restructured to include a paragraph on the effects of uncertainties, interferences, possible loss mechanisms in the cuvette ect.

2) The manuscript builds on measurements that are not described at all in the experimental section, such as the gas chromatography procedure and the ozone reactivity measurements. Particularly the latter one is troublesome as this seems to be an unusual measurement. There is no information on the measurement techniques whatsoever. Following the cited references it appears that UV absorption monitors were used for the ozone determination? This opens up the question if and how humidity was controlled for mitigating interferences that would be expected in the ozone measurement from the sudden changes in humidity (Wilson and Birks 2006) that are adherent with enclosure measurements, especially in situations when there is a switching back and forth between open and closed chamber conditions. I recommend that the parts about the ozone reactivity measurement be removed from the manuscript until the effect of changing humidity on the measurement has been well characterized and mitigated.

Since the focus here was on total OH reactivity emission rate measurements (our primary findings) and the comparison to the VOC-PTR-MS results, the GC-MS analysis and the analytical description of the total ozone loss rate approach was kept short. We agree with the reviewer that these details should have been included. This will be improved in the revised manuscript, especially in the experimental section. In both cases a short description of the technique will be added and a more detailed reference

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supplied.

Ozone was monitored by an analyzer of Horiba (model APOA-350E) which is based on UV-absorption. As the reviewer has noticed, this technique may show interferences caused by rapidly changing humidity as presented in Wilson and Birks 2006. The aforementioned study tested 4 UV-absorption ozone analyzers for their reaction to a sudden increase in the humidity. Relative humidity has been lifted from 0 to 90%. All tested ozone monitors showed an impact following this extreme test. The monitor, which was used in the presented study, was not part of these tests performed by Wilson and Birks 2006. Nevertheless, it was tested for humidity artifacts as well. Due to an internal heating system the impact of humidity variation in the sample is negligible. Additionally, the humidity changes inside the branch cuvette system showed a gradual increase of much smaller magnitude about 20% of the relative humidity maximum. This discussion will be included into the experimental section of the revised manuscript, as well as an example will be added as can be seen in Figure 2.

3) There are further parts where in my opinion interpretations build upon rather speculative assumptions (i.e. weighing of rate constants for determining a MT of SQT class reaction rate; benzene identification). These sections should be eliminated or realistic uncertainty estimates should be presented.

We don't agree that the assumptions are speculative. The weighted rate coefficients for monoterpenes and sesquiterpenes are based on specific GC-MS analysis for two different days in springtime and late summer. The observed speciation agrees with literature values and was discussed in detail in Section 4.3. Here also the impact of possible changes in the reaction rate coefficients due to changing compositions was fully discussed and found to improve the match between total OH reactivity emission rate calculations and measurements, but not to explain it completely. In the case of benzene the identification of this mass as benzene has been vindicated by previous comparisons (e.g. De Gouw and Warneke 2006). The references to these works will be added to the manuscript to further support the underlying assumption.

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As the referee suggests we will include a more detailed discussion of these uncertainties in the revised version.

4) 'Data' are always plural, so please correct all verb conjugations throughout the manuscript.

Okay, this will be made consistent.

5) Throughout the manuscript, including tables, data are presented in a rather large variety of significant figures, at times suggesting much higher measurement accuracy than what was achieved in these measurements.

A detailed discussion of uncertainties will be implemented in a revised version of the manuscript. As an example, the limit of detection for TOHRE will be provided, the uncertainty of the ozone monitored will be included, Section 4.3 will be extended to a detailed discussion of possible artifacts and uncertainties in the methodology. Significant figures will also be made consistent.

6) Spring is generally defined as March 21 – June 20. Please adhere to this definition or provide an explanation why it was disregarded.

The data-set was divided into periods for better interpretation and analysis according to the situation present in environmental and experimental conditions. This terminology will be specified and related to the meteorological seasons which define spring for the period March 1 to May 31 (e.g. Trenberth 1983).

7) 13500/28 Specify what type of 'flux' was observed.

The reviewer refers to a section in the introduction part. Here we give an example for the impact of biogenic emissions on measurements of total OH reactivity in forested environment. In Nölscher et al 2012b, the comparison of in and above canopy measurements in the boreal forest showed higher total OH reactivity inside the forest canopy for high temperature conditions. During the impact of heat the boreal vegetation emitted a multitude of biogenic compounds which likely contributed significantly to the measure-

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ments of total OH reactivity inside the canopy. By comparing individually determined OH sink compounds to the direct measurements of total OH reactivity, the unexplained fraction at that time was high. Those results will be clarified in a new version of the text.

8) Avoid using percentage or fractional scaling of temperature, as it is not clear if this figure relates to the Centigrade or Kelvin scale.

Ambient temperature is given in degree celsius (see for example Figures 3 and 6) which will be added in parentheses ($^{\circ}\text{C}$) to the text.

9) 13503/6 Kim et al (2009) show substantial loss of PTR-MS sensitivity in the measurement of higher molecular weight species such as for SQT compounds. This manuscript does not specify how corrections for SQT quantification were considered and what the uncertainty of the measurement was.

In fact, all quadrupole PTR-MS systems detect higher mass species with a lower sensitivity than lower mass species. This can be observed when performing a calibration or an ion transmission test. As described in detail in Boursoukidis et al (2012), the sesquiterpene signal was calibrated and uncertainties estimated. This is not part of our manuscript about total OH reactivity observations, since sesquiterpenes play only a minor role in the total OH loss rate budget.

10) 13504/22 Shouldn't the reactivity rate also be normalized to the dilution flow rate into the enclosure (resulting from the withdrawal of air by the gas monitors)?

Yes, this dilution was taken into account in the calculation of total OH reactivity emission rates, as explained in Section 2.4. Nevertheless, we will revise the text in this section to further clarify this procedure.

11) 13506/8 Isn't it super speculative to estimate a generic OH rate constant for SQT given the scarcity and high variability in published SQT+OH rate constants and the uncertainty in the SQT speciation of emissions?

We do not agree that the approach is speculative, for the following reasons: We are

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using published and reviewed reaction rate constants, we note that this generated uncertainty and we discuss the effect of possible changes thoroughly. While the reviewer has a point that the number of rate coefficients for sesquiterpenes with OH is rather limited, they are relatively similar to one another (differing by a factor of ca. 3). This is not the case for monoterpenes (which differ by orders of magnitude) which was why we undertook to determine their speciation by GC. For both monoterpenes and sesquiterpenes a weighted rate coefficient was derived based on this GC analysis. As stated already in comment No 3), we will include in a revised manuscript the detailed discussion of uncertainties.

12) 13507/2 What are 'no detectable' emissions? Please provide threshold values.

The limit of detection for TOHRE equals the increase in measured total OH reactivity during closure that cannot be differentiated from the noise of the instrument. The detection limit of the CRM is 3-4 s⁻¹ when calculating the 2 σ of the background noise. Assuming an increase about 3-4 s⁻¹ is just detectable by the instrument, the detection limit for TOHRE is 0.089 s-2g(dw)-1m-3. We thank the referee for this important comment, and we will add the threshold values as well as a description to the experimental section of the manuscript.

13) 13507/11 Definition of error margins (uncertainty range?) is missing here and elsewhere.

The given uncertainties of average values are standard errors (as explained in Table 2). This will be further clarified/defined in the text, as well.

14) 13509/26 Is 84% the relative missing fraction for late summer (as implied from the wording of this sentence)?

Yes, this will be clarified.

15) 13512/26 93% is not a factor.

This will be corrected.

16) 13513/15 There are obvious limitations of PTR-MS identification. Was the identity of benzene confirmed by GC-MS? If not, then this whole section should be eliminated.

At that particular day, no GC-MS analysis was deployed. The PTR-MS detected benzene on m/z 79. This mass is predominantly benzene, although compounds such as dimethyl sulfoxide, borazine and bromine in principal could also appear on that particular mass. However, benzenoid compounds are known to be emitted by vegetation in stress conditions as can be found in the literature (Heiden et al., 1999; White et al., 2009; Dudareva et al., 2006). We wish to retain the observation that this mass increased in the manuscript. We will point out that it may be another compound with the same mass to charge ratio although thus far in the literature comparisons with hyphenated techniques suggests this mass can be reliably identified as benzene. [Similar question arose by referee No1, please find here a similar answer.]

17) 13516/9-15 This explanation is not that clear and should be further detailed.

Since this section seems to be not well understood, we will rephrase it and add further discussion.

18) Figure 4: Were methanol, acetaldehyde, ethanol, acetone indeed quantified by GC-MS? Please provide these details.

Apologies for this misleading caption. Only monoterpenes and sesquiterpenes were measured with the GC-MS system in order to speciate the detected total monoterpene/total sesquiterpene signal, which was provided by PTR-MS. The sentence should be written correctly: "The composition of biogenic VOC emissions (measured by PTR-MS) and monoterpenes speciation (by GC-MS) for both measurement periods. . ."

19) Figures 6 and 8: Legends were too small and faint to be readable on a printout.

Yes, this will be improved.

Overall, the referee pointed out several important and crucial issues of the manuscript. These will be improved and corrected in a new version. Figures and text will be revised

according to the referees comments.

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

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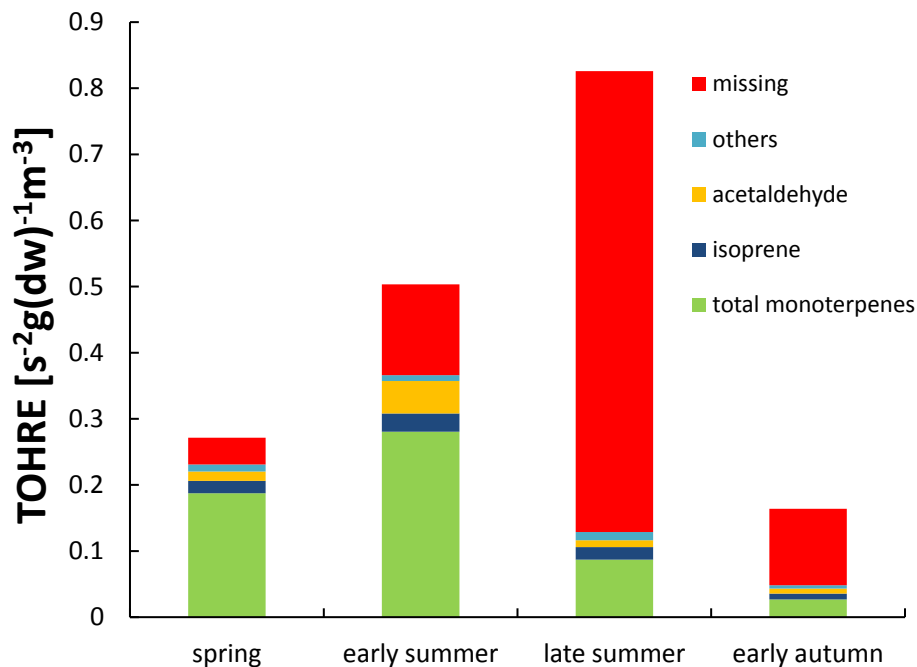


Fig. 1. Averaged TOHRE for the 4 defined periods: spring (24 May–31 May 2011), early summer (01 June–14 June 2011), late summer (12 Aug–26 Aug 2011) and early autumn (27 Aug–07 Sept 2011).

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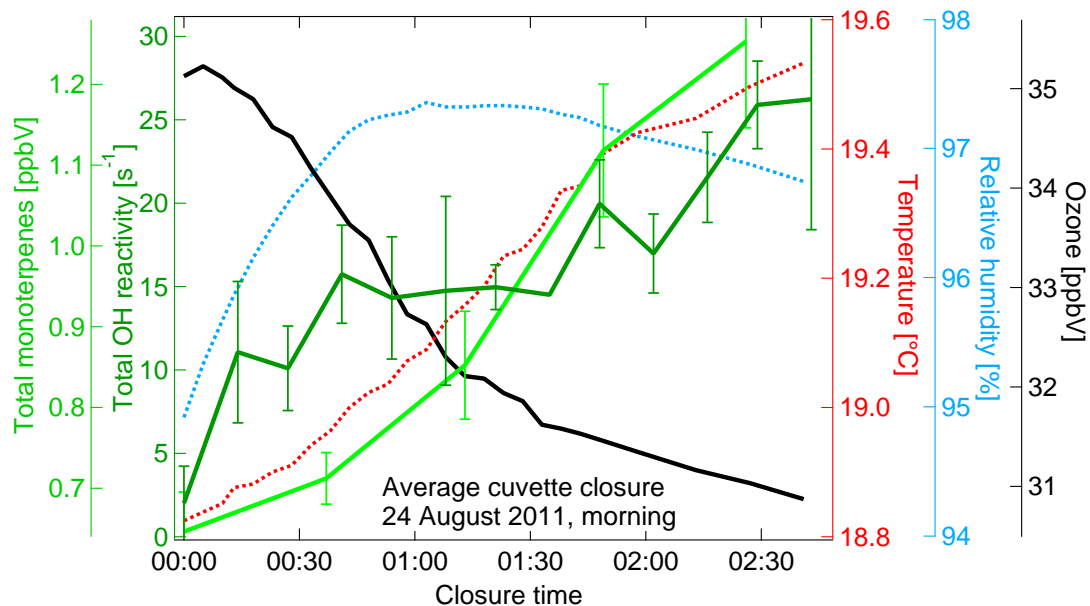


Fig. 2. Example of VOC-PTR-MS (total monoterpenes), CRM (total OH reactivity) and sensor (temperature, relative humidity, ozone) signals inside the cuvette during closures.

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