

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.

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We are grateful for the helpful comments of the referee. In the following text, these remarks are discussed and answered. The manuscript will be revised accordingly.

1. While considerable ozone consumption was measured, some of which occurred in reactions with terpenes, sesquiterpenes, the reaction products of these are not included in the calculation of OH reactivity from individual species observed (see Kim et al 2011). These reaction products (2nd and 3rd generation) are probably too sticky to be quantitatively (or even qualitatively) detected by PTR-MS or GC-MS techniques, so that their concentrations and identities must be inferred. Why is this not included in the

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discussion?

The referee suggests inclusion of a discussion of possible products from ozonolysis inside the cuvette. Other referees have also drawn our attention to this point and so this discussion will be added to the revised version. Bourtsoukidis et al (2012) discussed in detail all the relevant loss processes inside the cuvette system. They found that especially the emitted sesquiterpenes reacted with ozone. This effect on the measurement of the total sesquiterpene flux was corrected for by the method described in Bourtsoukidis et al (2012). The estimated loss rate of sesquiterpenes to the reaction with ozone was taken as $k(\text{SQT}+\text{O}_3)=(6.6\pm 2.1)\times 10^{-15}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$. For all other detected compounds the chemical degradation inside the cuvette was a minor effect. E.g. the signal of monoterpenes was corrected with $k(\text{MT}+\text{O}_3)=(9.4\pm 2.1)\times 10^{-17}\text{ cm}^3\text{ molec}^{-1}\text{ s}^{-1}$. The VOC-PTR-MS data was also corrected for deposition ($k_{\text{dep}}=(2.64\pm 0.23)\times 10^{-5}\text{ s}^{-1}$). Deposition and loss due to ozonolysis were minor when compared to the effect of dilution ($k_{\text{dil}}=(2.9\pm 0.2)\times 10^{-3}\text{ s}^{-1}$, see comment No 2).

Nevertheless, ozonolysis of the tree emissions in the gas-phase as well as surface reactions on leaves potentially form products. If these products are too sticky to be detected by PTR-MS or GC-MS techniques, as the referee suggests, they are as well too sticky to be measured via CRM, as the systems employ the same inlet.

In general, the total OH sink budget for the Norway spruce direct emissions would only be affected by ozone consumption inside the cuvette if:

a) A compound reacts as fast with ozone as with OH, so that the two reactivities compete for each other. In this case, the measured TOHRE will be underestimated, since the increase inside the closed cuvette due to the direct emission of this compound would be reduced.

b) Through the reaction with ozone highly OH reactive secondary products significantly build up within the cuvette. However, because of the short closure time of 3 minutes

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these products levels have to increase at rates similar to the primarily released tree emissions, in order to impact the direct measurement of TOHRE.

c) The ozonolysis produces significant amounts of OH. This would cause an underestimation of both, the measured and calculated TOHRE.

These points will be discussed in the revised form of the manuscript. Similarly to the discussion of the rate constant for mono- and sesquiterpenes in the calculation, an analysis of other possible interferences and obstacles of the reported observations will be included in the revised manuscript.

2. Ambient air is continuously leaked into the enclosure to replace air withdrawn for analysis by PTR-MS, GC-MS ozone analyzer ect. The estimated leak rate is not given, but may be significant. This air contains fresh ozone and OH, which likely react with terpenes and sesquiterpene emissions. Please discuss.

Indeed, the air withdrawn by the instruments (about 1.7 l/min) leaked into the cuvette during closure and diluted the air sample. The dilution factor was calculated to be $k_{dil} = (2.9 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ and was applied to the measured total OH reactivity (as described in the manuscript on p. 13504, l.16). The influence of ambient OH is negligible, as it is very reactive (with a lifetime of several ms) and tends to be lost on orifices and tubing at such low flow rates. It therefore does not impact VOC and total OH reactivity levels. Ambient ozone, which was possibly drawn into the cuvette, did not significantly differ from the levels inside the closed system. The ozone levels decreased during closures with a factor of several pptV s⁻¹. Overall, the dilution of measured mixing ratios and total OH reactivity was considered within the analysis. Possible entrainment of oxidants is of negligible importance for the applied cuvette system.

3. The estimation of monoterpenes and sesquiterpene emissions used only temperature dependent algorithms. Some of these emissions may have had a significant light and seasonal dependence. Was this explored (it has a direct effect on your results?)

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Yes, a temperature and light dependent algorithm was tested as well. The comparison to measurements of TOHRE showed a mismatch during the nights. Here total OH reactivity emission rates were higher, than predicted by the light driven algorithm. However, the temperature-only dependent algorithm was used in order to focus on the temperature-driven release of VOCs which is considered to be predominant for Norway spruce. The intention of this study was predominantly to highlight significant deviations from the temperature-only driven emission algorithm. This way, several events could be studied in more detail such as the mechanical stress during storms, heat stress, and seasonality. These characteristic events could be explored in terms of their importance to total OH reactivity fluxes. For clarification we will rephrase this paragraph and add a sentence concerning the light and temperature dependent algorithm.

4. No evidence is provided to support the statement that no UV light penetrated the cuvette walls to induce photochemical reactions. Please provide this.

This will be done in a revised version of the manuscript (see e.g. Krizek et al 2005).

5. Ambient temperature is not plotted alongside the cuvette temperature to allow the judgement of cuvette temperature increases during the closed-cuvette measurement period (it is not clear how long the cuvette was closed during the OH reactivity measurements). Certainly ozone consumption increased with cuvette temperature and is assumed to relate to chemical losses (which may have also resulted in some OH production). Again, the products of the chemistry indicated are not included in the theoretical calculation of OH reactivity as the sum of the individual reactants with OH.

Similarly to comments No 1 and No 2, the referee points out possible difficulties of the method used for the flux measurements used in this study (such as increasing temperature and its effect on chemical reactions inside the cuvette). During the 3 minute closures (noted in the manuscript on p.13502, l.10), the temperature generally did not increase by more than 10 % in degree celcius (°C).

Ozone inside the cuvette will react with the reactive double-bonded emissions of the

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Norway spruce branch. Reaction rates are fastest with sesquiterpenes and monoterpenes. This loss was accounted for in the calculation (which will be further clarified in the revised manuscript). Further ozone reactions and possible OH production are of minor impact at the timescale of 3 minutes. The calculation of a theoretical total OH reactivity flux is based on the compounds, that have been detected by PTR-MS as shown in Table 1. These include the major known primary emissions of Norway spruce such as monoterpenes, acetaldehyde, isoprene, and acetone. All other compounds, which are reactive to OH and possibly also emitted by the tree but not detected within the PTR-MS, are candidates to increase the level of this calculation.

In addition to the presented example for total OH reactivity measurements inside the cuvette (Figure 2, manuscript) we will give an example for other parameters measured (in addition to total OH reactivity) during closure (Figure 1, attached to this answer). This will clarify the rate and absolute increase of temperature and humidity, as well as the linear slope of e.g. the total monoterpenes. The shape of the primary biogenic emissions increase in contrast to the decrease of ozone provides additional evidence for no significant interference of reactions inside the cuvette.

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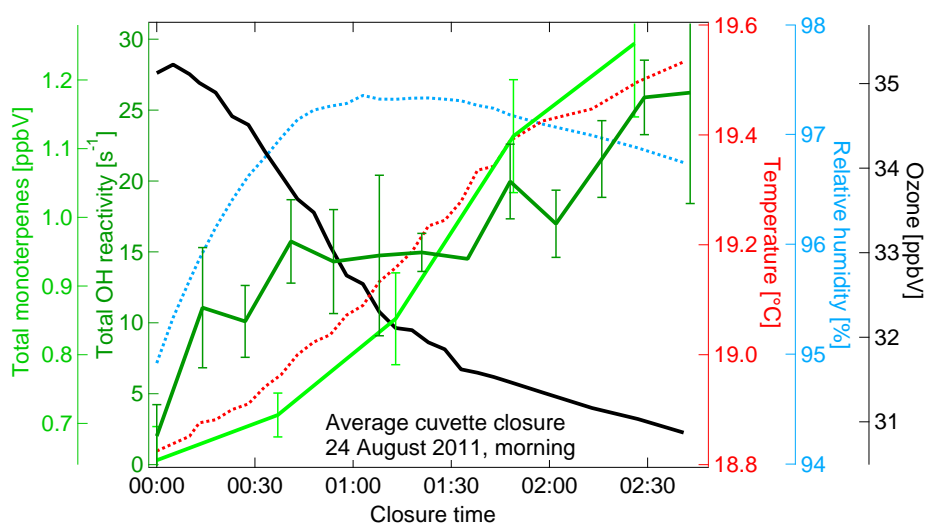


Fig. 1. Example of VOC-PTR-MS (total monoterpenes), CRM (total OH reactivity) and sensor (temperature, relative humidity, ozone) signals inside the cuvette during closures.

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