Reply to Referee #1

We thank Anonymous Referee #1 for their helpful comments. We have answered to the comments below. The bold text is quoted from the referee's comments, and the text in italics has been added to the manuscript.

GENERAL COMMENTS

The manuscript entitled "Simple proxies for estimating the concentrations of monoterpenes and their oxidation products at a boreal forest site" by Kontkanen et al., describes a method to calculate the mixing ratio of monoterpenes and their oxidation products using a simple proxy method. The method was applied to a huge data set from 2006–2013. I recommend publishing in ACPD after addressing the following issues.

The manuscript is very interesting and well written. It contains a clear description of the proxy method. However, some information are still missing, in particular details about the PTR-MS measurements. A clear description how the measured concentration of monoterpenes and their oxidation products was obtained is missing. The description should address the following points:

1) What is the definition of [MT]$_{measured}$?

2) Which compounds were considered for PTR-MS measurements to obtain [MT]$_{measured}$?

3) How was the PTR-MS calibrated and which compounds were used for calibration?

4) Are the data of the PTRMS corrected for temperature and RH dependency? This might be very important for summer and winter measurements.

5) How was the concentration of monoterpenes and oxidation products calculated?

6) Oxidation products have often a different response factor than their precursor compounds. Was this considered for calculation?

As suggested by the referee we added a more detailed description of the PTR-MS measurements in Section 2.1:

The PTR-MS was maintained at a drift tube pressure of 1.95–2.20 mbar. The primary ion signal (H_3O^+) varied between 1 and 30×10^6 cps, being typically around 10×10^6 cps. With these settings, the E/N ratio where E is the electric field and N the number density of the gas in the drift tube, varied between 105 and 125 Td (Td = 10^{-21} V m^{-2}). The instrumental background was determined every second or third hour with a zero-air generator (Parker ChromGas Zero Air Generator, model 3501, USA), and the instrument was calibrated every 2–4 weeks using an alpha-pinene standard gas (Apel-Riemer Environmental Inc., USA, or Ionimed GmbH, Austria) which was diluted to around 1–5 ppbv. The monoterpene concentrations were derived from the measured m/z (mass-to-charge ratio) 137 signal according to Taipale et al. (2008). Shortly, the measured signal was first normalized using measured H_3O^+ and $H_2OH_3O^+$ signals, and the drift tube temperature and pressure. Then, the normalized signal was converted to the volume mixing ratio using a normalized instrumental sensitivity.

In addition, the answers to the referee's specific questions are below:

1) [MT]$_{measured}$ is defined as the measured monoterpene concentration (see the next point) in units molecules cm^{-3}.

2) The measured monoterpenes are detected at *m/z* 137. This sums up all monoterpenes as well as other compounds with molecular mass of 136 amu and proton affinity higher than that of water because the PTR-MS is unable to distinguish between compounds with the same molecular mass.

3) The calibration gas included alpha-pinene as a representative monoterpene. It is well justified since alpha-pinene is the most common monoterpene found in ambient air in boreal forest (e.g. Hakola et al., 2009). The calibration was conducted as described in Taipale et al. (2008). In short, calibration gas containing 1 ppmv of alpha-pinene was diluted close to typical atmospheric concentrations using zero air generator based on catalytic conversion (Parker ChromGas Zero Air Generator, model 3501, USA). The calibration was conducted 2–4 times per month.

4) PTR-MS data were not corrected for temperature and RH. Ambient air was drawn to the PTR-MS through a heated sampling line, and the measured monoterpene concentration was considered to represent the ambient monoterpene concentration at the measurement height under all temperature and RH conditions.

5) The concentration of monoterpenes was calculated following the scheme described in Taipale et al. (2008). The measurements of monoterpenes oxidation products were not utilized in this study.

6) As mentioned in the previous point, the measurements of monoterpenes oxidation products were not used.

MINOR COMMENTS

Page 3, line 10: The authors stated that few data were available which were obtained during measurements campaigns. Is there any comparison of the PTR-MS with other methods/instruments to validate the PTR-MS data?

In Ruuskanen et al. (2005) PTR-MS measurements were compared with GC-MS (gas-chromatograph mass spectrometer) measurements at the SMEAR II station. A reasonable agreement was found between these methods in monoterpene concentrations over a period of several months. More recently, Kajos et al. (2015) compared the concentrations of oxidized and aromatic VOCs (methanol, acetaldehyde, acetone, benzene and toluene) measured by two PTR-MS and two GC-MS instruments in ambient air at the same site. A very good correlation between different methods was obtained for benzene and acetone.

Page 4, line 13: The approach considers reaction with O_3, OH and NO_3 as well as condensational sink. Is there a reason that the photolysis is not considered for the calculation? In particular, this might be very important for oxidation products such as pinonaldehyde, nopinone etc.

Regarding this comment, as well as the comments below, it is important to note that in our calculation we do not consider any reactions for the first-generation oxidation products but we assume that they are further oxidized until they are condensable. Therefore, we also did not include the photolysis of oxidation products in the calculation. This was, however, not clearly enough explained in the text and therefore we added the following sentences to the manuscript in Section 2.2.2:

It should be noted that OxOrg can be thought to represent the total concentration of oxidized monoterpenes, because it takes into account all the generations of oxidation products, from the first oxidation until condensable molecules. However, as the formulation of this proxy presumes that oxidation takes place relatively fast and that there are no others sinks than condensation sink, it should be considered as a rough estimate for the concentration of condensable organic vapors.

Page 28, Figure 9: According to the calculations O_3 is the most important sink for monoterpenes as well as for monoterpene oxidation products. This is surprising as the rate constant for

OH+monoterpene is in general much faster than with O₃. What is the reason for this observation?

It is true that these results indicate that the oxidation by O_3 is the most important sink for monoterpenes. However, this can be explained by the fact that O_3 concentration is orders of magnitude higher than OH concentration. The median OH concentration (estimated from a proxy for times when there was solar radiation) was 2.4×10^5 cm^{-3} while the median O_3 concentration for the same times was 8.2×10^{11} cm^{-3}. Regarding monoterpene oxidation products, we do not analyze the relative importance of their reactions, as explained above.

Furthermore, it was stated that a-pinene is the most important monoterpene. The first-generation oxidation product is pinonaldehyde. As pinonaldehyde does not contain any C-C double bond it cannot react with O₃. This is the same for few other oxidation products like nopinone. Why is OH radical reaction not considered for monoterpene oxidation products?

As explained above, we do not consider any reactions for the first-generation oxidation products.

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