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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.

Anonymous Referee #3

Received and published: 29 November 2012

This article presents seasonal measurements of OH reactivity in emissions from Norway spruce, which makes this a rather unique data set. To my knowledge comparable measurements have not been presented elsewhere before. This manuscript is a timely contribution, as there has been a growing interest in better defining the reactivity of emissions from vegetation in the attempt to better understand observed discrepancies between measured and modeled chemical reactivities in forest air.

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 ACP standards. I find

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the organization of the manuscript unfortunate. A more succinct presentation showing 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 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 technique 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 the changing humidity on the measurement has been well characterized and mitigated.

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. Other general comments:

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

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.

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

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Other specific comments:

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

13502/13: Avoid using percentage or fractional scaling of temperature, as it is not clear if this figure relates to the Centigrade or Kelvin scale.

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 in the measurement was.

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)?

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?

123507/3: What are 'no detectable' emissions? Please provide threshold value.

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

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

13512/26: 93% is not a factor.

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.

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

Fig. 4: Were methanol, acetaldehyde, ethanol, acetone indeed quantified by GC/MS? Please provide those details.

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Fig. 6: Legends were too small and faint to be readable on a printout.

Fig. 8: Same as Fig. 6.

Wilson, K.L. and Birks, J.W. (2006) Mechanism and elimination of a water vapor interference in the measurement of ozone by UV absorbance. *Environ. Sci. Technol.* 40, 6361-6367.

Kim, S.; et al. (2009) Measurement of atmospheric sesquiterpenes by proton transfer reaction-mass spectrometry (PTR-MS). *Atmos. Meas. Tech.* 2, 99-112.

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