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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 raised several important questions concerning the submitted manuscript. The critical discussion is acknowledged and will be answered in detail as follows:

1) My understanding after reading the current form of manuscript is that there was ozone in the air flowing in the cuvette system for ozone loss quantifications. If that is the case, chemical transformation of BVOCs is expected. This is especially true for monoterpene and sesquiterpene species which have high ozone reactivity. This also means that the air coming out from the cuvette might contain significant oxidation products from terpenoid-ozone reactions. If this is the case, the whole arguments

based on the assumption that observed missing OH reactivity is coming from primary emissions are not relevant anymore.

The products that may form from ozone reactions are most likely sesquiterpene (or monoterpene) products. Sesquiterpenes themselves contribute to less than 1% of the total OH reactivity emissions. In order to affect our measurements the products need to build up quickly (with a similar rate than the primary emissions increase during cuvette closure), must be very reactive to OH (even more than their "mother" compounds) and not as reactive to O3. In addition, these products need to be not too sticky to be detected. This is in principle possible, but rather not likely.

A small calculation using the chemistry degradation model MCM3.2 (http://mcm.leeds.ac.uk/MCM/) shows the following: Initial conditions are assumed with ozone levels of 20 ppbV and β-caryophellene of 300 pptV. β-caryphellene accounts for about 35% of the total sesquiterpene signal which varied in the measurement period between a couple of pptV up to 500 pptV during cuvette closures. The initial concentration of 300 pptV is an upper limit estimate, which corresponds to an OH reactivity of 1.5 s-1. The initial OH concentration inside the cuvette is chosen to be zero, since all OH present in the cuvette would be immediately reacted away or deposited to the surfaces. The reaction time in our closed cuvette system is 3 minutes. According to MCM3.2 the most important product of the ozonolysis of β-caryphellene is BCSOZ, which increases up to 100 pptV after 3 minutes. In terms of OH reactivity this product accounts for 0.18 s-1, whereas the resulting 100 pptV of β-caryphellene after reaction with ozone account for still 0.5 s-1. Hence during the time of closure, about 1 s-1 /3 min OH reactivity is lost in the signal due to the direct emission (of β-caryphellene) and about 0.18 s -1/3 min OH reactivity increase is gained due to the products. This simple calculation of a very reactive case shows the insignificance of the products formed inside the cuvette closure in comparison to the direct biogenic emissions. In general, the design of cuvette and experiment favors results (in terms of TOHRE) that are slightly underestimated. The measurements of TOHRE are based on the significant increase of the directly emitted reactive biogenic compounds. Loss processes potentially reduce this increase, but unlikely form products that rise in comparable rates. The net effect is a conservative measurement of the total OH reactivity emission rate from the enclosed branch.

In the revised manuscript this comment will be discussed in detail.

2) As the authors described, the observed ozone losses are expected from not only chemical losses but also wall and stomatal uptakes. The authors admit that they could not separate ozone loss rates from each process but still discussed about the data in the context of chemical ozone losses from unknown chemicals without any justification. The authors should either withdraw the presentation and discussion of the ozone loss observation dataset or throughly discuss for the justification of physical meaning of the dataset.

The observed total ozone loss rates were discussed carefully and we studiously avoided talking about total O3 reactivity. The intention was to compare diel profiles and trends in order to provide as comprehensive assessment of the data as possible. We prefer to keep the ozone discussion in the paper for completeness and so we will augment the discussion of this value inserting the appropriate caveats. This will include:

Empty cuvette tests found the wall loss of ozone to be stable in time and of minor importance (less than 6 pptV/s). Following, the variations in the observed total ozone loss rates are caused by either uptake to the needles or total O3 reactivity. Both loss processes are driven biogenically and hence of interest for our data-sets interpretation. Nevertheless, the discussion about total ozone loss rates needs to be handled with care and we will rephrase the manuscript for more clarification.

In order to de-emphasize the presented approach of ozone loss rate observations, we will change the title of the manuscript to: "Seasonal measurements of total OH reactivity emission rates from Norway spruce in 2011".

3) By definition, OH reactivity is reciprocal of lifetime of OH with the unit of time and flux is "the rate of flow of a property per unit area". I understand that the authors try to develop a term that represents reactivity of BVOC emissions but I would argue that the new term that the authors developed actually is very confusing and may be physically incorrect. The authors could simply describe that the amount of missing BVOC emission is equivalent of x times of alpha-pinene emissions. This way, readers would not need to consume time to learn about the confusing new term.

We understand that the concept of total OH reactivity seems to be confusing at first sight. And the application of total OH reactivity as emission rate, maybe even more. However, we do not understand why this new term could be physically incorrect.

TOHRE is the total OH reactivity emission rate. Emission rates are defined as mass of a compound per unit dry leaf mass per hour. Based on this definition we concentrate on the emitted OH reactive compounds per unit dry leaf mass per hour. Since we are interested on the effect of the tree emissions on OH, we need to define the total OH reactivity per unit dry leaf mass per hour and volume. The volume is necessary since we cannot calculate a mass of these OH sink compounds. Measuring total OH reactivity as total OH sink provides the budget of all of these compounds. It is impossible to define a number, mass, or composition of this total OH sink via our measurement method.

We agree that a calculation of an α-pinene emission equivalent to the missing TOHRE could be useful and interesting. This way, the reader would get an idea of the amount of missing OH sinks being directly emitted by the Norway spruce in terms of a familiar molecule.

The referee is thanked for the critical review. According to the comments we will improve the manuscript and clarify descriptions and concepts.

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