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Biogeosciences Discussions

Interactive comment on "Ozone stress as a driving force of sesquiterpene emissions: a suggested parameterization" *by* E. Bourtsoukidis et al.

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We would like to thank anonymous referee #2 for acknowledging the importance of the study and for proving us insightful and fruitful comments that will improve the quality of the manuscript. We agree that the limitation to one branch only is certainly notable but was the only way to investigate the effect of ozone by current means. The main goal of the study was to examine the seasonal behavior of SQT emissions. Different trees, considering the variability among tree types, might have caused a deeper look into the variety of the data from a tree or an ecosystem. This will be addressed in future collaborations and studies. With respect to this study we took into consideration all of his comments and detailed answers/revisions to the points made can be found below. One should notice that anonymous referee #2 is referring to a previous version of the

manuscript (as originally submitted to Biogeosciences) and therefore the pages and lines of his comments are also converted in the on-line discussion version.

Page 3 Line11 (page 7664 Line 15) : non-stomatal instead of nonstomatal Corrected

Pag 3 Line 20 (page 7664 Line 23): you may want to consider to cite Jardine et al. 2012 (GCB), where emissions of oxidation products from leaves in demonstrated.

The citation of Jardine et al.2012 is added in the revised version.

Pag 4 line 30 (page 7666 Line 17): remove "an" and use "a".

It is already corrected in the BGD manuscript.

Pag 4 line 30 (page 7666 Line 17): did you focus the all study using just one branch? Which was the leaf area of the enclosed branch?

The comment is certainly of interest for plant exchange. After considering anonymous referee #1 comments in the first evaluation of the manuscript, we added more information concerning the branches used (Page 7667, Lines 5-15). Unfortunately the leaf area of the enclosed branch was not quantified directly. However the biomass enclosed was quantified and general relations of amount of needles per g dry weight was gained. A first order approximation could be made for request. Since this value is only an approximation with a notable uncertainty we skipped any consideration of the leaf area for this particular study.

Pag 5 line 9: what was the material of the enclosure? Did you test if it ozone and other reacting gases interact with cuvette walls?

"The dynamic branch enclosure was a cylindrical shaped glass cuvette" (Page 7667, Line 5). Ozone and NO have been checked for wall loss rates (empty cuvette) but were found to be negligible during the period of closure. We will add the following sentence on Page 7667, Line 11:

"Interaction of ozone and other gases were studied in order to quantify possible inter-

ferences with the enclosure. Ozone did not show to react with the cuvette's wall while VOCs were corrected for deposition."

The deposition term is described in detail at the emissions calculation section (Page 7671, Line11)

Pag.5: Please specify in the Experimental set-up session the measuring period.

We added the following sentence (Page 7666, Line 17):

"The measurements took place from 8th of April to 11th November 2011."

Pag 6 line 14: Did you calibrate SQT using just m/z 205 or you considered other fragments? This is reported in the next section although it should be mentioned here. Pag. 7 line 4: m/z 149 has been previously associated to Methyl-Chavicol (Bouvier-Braun et al. 2009). Can you exclude interference of this compound with the SQT fragment?

SQT were calibrated considering the complete fragmentation pattern. However for the results presented in the study we considered only the parent ion mass (m/z=205) to avoid interferences of methylchavicol. This is stated on page 7668, Line 23(Page6 line 20) : "The relative abundance of parent SQT ion signal quantified as 32$\pm$2% and comes in line with the previous values reported."

Pag 9 line 6 (Page 7672, Line 19): Guenther and not Guether.

Corrected.

Pag 9 equation 2 (Page 7673 Line 6): can you provide more detail on how the two unknown terms in the equation were calculated?

We will added the following sentence in order to make it more clear :

"The two unknown terms were calculated by the exponential fitting between temperature and SQT emissions."

Pag 10 lines 14-19 (Page 7674 Lines 14-19): given the dependence of ozone with tem-

perature, it is expected a certain correlation between SQT emission and ozone, this is not surprising. You should remove the effect of covariates before analysis regressions between ozone and SQT. Perhaps trying a step-wise multi-regressive approach may help.

We would like to thank referee #2 for this excellent comment and insightful idea.

We would suggest enriching Fig. 4 with the step-wise calculated correlation coefficient between temperature and ozone. In this way, the reader would clearly recognize the correlation between these two parameters, which is getting weaker in elevated ozone concentrations for the site of interest. This is clearly an effect of anthropogenic pollution arriving from the Rhine –Main industrialized area. Therefore, we would suggest using the figure attached in the supplement with the enriched caption and text:

Caption: "Correlation coefficients for temperature and ozone calculated individually for ten different ozone regimes. In moderately or less polluted atmospheric conditions SQT emissions were better correlated with temperature, while in more polluted atmospheric conditions the emissions were better correlated with ambient ozone mixing ratios, indicating a critical threshold in the parameter that is driving the emissions. The smaller correlation between ambient ozone concentrations and temperature is observed in higher ozone regimes, indicating a stress due to ozone only not because of heat stress."

We will also add the following paragraph:

Text (Page 7678, Line 22): "Ozone is produced in the troposphere by the tropospheric VOC-NOx-radiation cycle (Seinfeld and Pandis, 2006) via the conversion of NO to NO2 and the subsequent the photolysis of NO2. Since radiation and temperature are strongly coupled, both parameters show a dependency with ambient ozone concentrations. Fig 4 is also demonstrating the correlation coefficient between temperature and ambient ozone concentrations. In less polluted regimes the correlation is higher indicating the natural formation of ozone molecules without the subsequent destruction of

ozone by elevated levels of NOx. However, in more polluted regimes the given correlation is showing the tenancy to decline. This is attributed to the anthropogenic pollution arriving from the highly populated and industrialized Rhine –Main area. Therefore, the increased dependency shown for ozone in higher regimes, is not strongly associated with the temperature effect in SQT emissions."

Pag 12 line 2 (page 7676 Line 17) : younger leaves usually have thinner cuticles. SQT emissions may come from MVA pathway but may also leak out from resin ducts, therefore leaf phenology may have an effect on SQT release from needles/branches.

Agree. But it might also be that SQT are not stored inside the needles but somewhere else as the bark or the roots. After a rough calculation and using literature values for stomata conductance (F.Loreto; personal communication) we did not find any SQT pools inside the leaves. However, the calculations remain speculative without measures of physiological parameters and therefore were excluded from the material of the paper.

Pag 12 line 10-13 (page 7676 Line 26): It is unclear why you say that during the growing period Est declined. It seems to me form figure 2b that low Est were observed outside the growing period.

In the revised manuscript we will define the growing period lasted from 26.04.2011 to 09.05.2011 so it is easily recognizable by the reader.

"During the growing period (26.04.2011 to 09.05.2011) Es(T) was dramatically reduced as was the β-factor. An explanation for the reported low values could be that newly grown leaves have different SQT capacities and therefore react different to environmental factors until they become mature."

Pag 12, correlation coefficients: Low ozone concentration does not correlate well with SQT emission, this may be due to the limited oxidative damage when ozone is low. However, showing good correlation between ozone exposure and SQT emission per se

cannot justify the statement that ambient O3 concentration can be harmful for Norway spruce. I would have appreciated some data on plant ecophysiological parameters to support this thesis.

Unfortunately plant ecophysiological parameters could not be measured due to the limitation in instrumentation. This will certainly be addressed in future cooperation. However the exact sentence (Page 7677 Lines 23-24; "This indicates that ambient ozone concentrations can be substantially harmful for Norway spruce above a critical threshold") is formed in a speculative manner. Nevertheless, the addition of the CC between temperature and ozone shows that SQT emissions are highly correlated with ozone, not because of the temperature effect but mainly due to ambient ozone concentrations.

Pag 13 lines 18-19: Again, oxidative stress is mentioned without proving any oxidative damage, this sentence is too speculative.

The referee is probably referring to the phrase (page 7678 Lines 14-15) "For ozone concentrations between (36.6 and 52.2$\pm$0.3) ppbv the strength of these two driving forces was relative stable, with the indication that oxidative stress was more important than the heat stress." By the term "oxidative stress" we wanted to define SQT emissions triggered by ambient ozone concentrations. Similar, "temperature stress" does not show any damage to Norway spruce but this terminology is used to describe the temperature effect.

In the revised manuscript the sentence will be rephrased as following:

Page 7678 Line 13: "For ozone concentrations between (36.6 and 52.2$\pm$0.3) ppbv the strength of these two driving forces was relative stable, with the indication that ozone is more important SQT emission driver than temperature."

1)Page 14 line 13 (Page 7679 Line 14): who says that MT emissions are not a usefull proxy for oxidative stress? 2)Page 14 line 14 (Page 7679 Line 17): what is a dynamical well? You mean a bell shape? Please explain. 3)Please rephrase the all paragraph

between lines 14 and 18. I don't see differences between MT and SQT emission potentials for ozone regimes above 47.7 ppb.

1) We agree with this comment. MT could be a useful proxy for oxidative stress as it is mentioned just above discussing the results of regression tree analysis. However, if the MTs consist primarily of camphene, they are no good proxy for ozone stress. It essentially depends on the chemical composition of individual MTs within the emissions. Since at the site of interest MT consist dominantly of MT reacting primarily with OH but much less with ozone they cannot be considered to be critical for ozone stress What we intended to indicate is that along the complete ozone spectrum both Es and ïĄć-factor are relative constant. This is caused by the primary MT, which is ïĄć-pinene that mainly reacts with OH but only to a smaller extend with ozone. Therefore, the sentence will be rephrased as following: "However, at the site of interest MT consist dominantly of MT reacting primarily with OH, but much less with ozone, so they cannot be considered to be critical for ozone stress"

2) What we actually mistranslated is the "potential well". In physics this is a well-known curve indicating the more energetically stable regime(s). As we mention in page 7674 line 9 "The 50% of annual measurements were situated between 23.2 to (57.1±0.3) ppbv." The Gaussian distribution of Es,SQT showed that the minimum emissions were observed in the most abundant for the ecosystem ozone concentrations.

3) One could recognize the difference between MT and SQT emission potentials for the last three regimes if considers the different scales. MT emission potential is almost four times higher. However, the referee is probably referring to the linearity that could be observed in the last three regimes. Our response will focus in the errorbars that indicate a steady Es and ïĄć-factor for MT, maybe apart for the last regime.

We will rephrase the paragraph as following :

"Emission potentials showed a similar behavior. Es,MT was almost constant for the majority of ozone regimes, with the highest values to be observed at the edges of very

clear and very polluted conditions. Regression tree analysis (Breiman et al., 1984) between ozone concentrations and MT emissions showed that MT are emitted in larger amounts when ambient ozone concentrations are above (54±4) ppbv. Therefore, MT emissions could be also influenced by ambient ozone concentrations but with a higher critical threshold. On contrary, Es,SQT displayed a potential well along the ozone spectrum and the lowest values were once more obtained for the range with the most representative ozone concentrations for the ecosystem at this site. For the regimes above 47.7 ppbv, Es,SQT rises linearly with ozone, stressing out the importance of this environmental parameter as a driving force of SQT emissions."

Pag 15 lines 19-21 (Page 7678 Line 1). No need to explain again what the coefficients in the Guenther algorithm are.

We would prefer keeping the detailed explanation of all coefficients so the reader can have all the information gathered.

Pag 16 line3: responses and not responces.

Corrected

Pag.17 lines 5-7 (Page 7682 Line 28): Please rephrase this paragraph, it is unclear. Moreover, I don't understand why storage pools should decrease during the year. More mature and thicker leaves should store more SQT. If you intend to keep this sentence, please provide a reference.

This comment comes in line with the earlier comment referring to Page 12 line 2 (page 7676 Line 17). "More mature and thicker leaves should store more SQT". That would be the case if SQT were indeed stored inside the leaves and if the emission intensity is less or equal to the production intensity. Since Bäck et al. (2012) found SQT below the bark, we consider that SQT are not stored inside the leaves only and daily calculated emission potentials (Fig2b) support this statement. Experimentally determined Es values show a clear exponential decline during the end of the year for identical tem-

perature conditions. If the storage pool or the basal emission rate would be constant throughout the year, this wouldn't be the case. Wintertime measurements should have provided us with more information. but due to the usage of purified liquid water for the PTR-MS measurements were impossible during that period.

Pag 17 lines 29-30: assumed that ozone has an effect on SQT emission, to prove oxidative stress photosynthetic parameters should be measured before using global simulation models for oxidative stress on plants. However, atmospheric chemistry models will benefit of your finding for producing a better estimate of SQT emissions.

We agree that photosynthetic parameters should be measured as well. We hope that this study will be a base for future even more detailed studies by a consortium of research groups to work with this very important VOC emission. Similar observations in other ecosystems are definitely needed in order to confirm this important observation and parameterization.

By applying all corrections as well as modifications as suggested by reviewer #2 we hope to have improved the manuscript in that way so that it can be accepted for final publication in Biogeosciences. Thanks to the reviewer for his excellent comments especially with respect to the statistical suggestions and plant physiological aspects.

Interactive comment on Biogeosciences Discuss., 9, 7661, 2012.

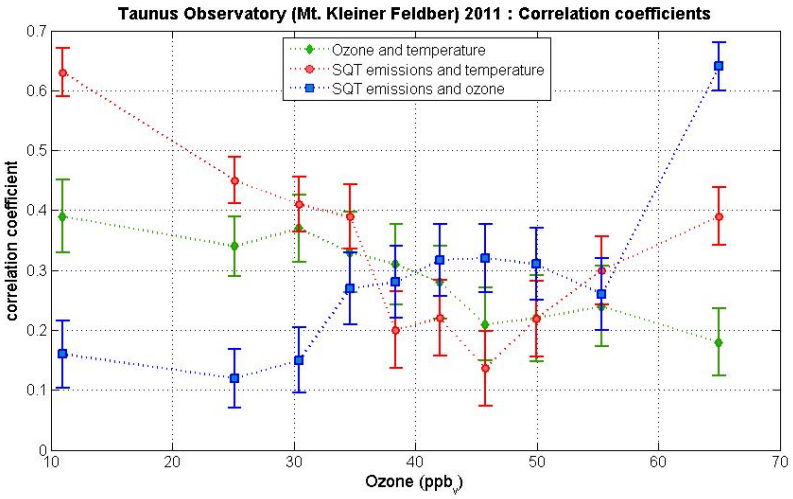

Fig. 1.