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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 #3 for his comments. We will try to address all the questions raised in detail.

RC:The manuscript is generally well written but needs careful editing to correct a few spelling errors (e.g., page 12, line 27 enchased should be enhanced; page 13, line 10 individual should be individually; page 16, line 3 responces should be responses; page 16 ,line 12 "found" should be "was found"; etc).

AC:Thank you. The mistakes mentioned were corrected as listed below. Page 12,Line 27 (page 7677,Line 6) : changed to "enhanced" Page 13,Line 10 (page 7678,Line 6) : changed to "individually" Page 16,Line 3 (page 7681,Line 18): changed to "responses"

Page 16,Line 12 (page 7682,Line 2) : changed to "was found"

RC:More importantly, there are some issues with references that don't seem to say what the authors imply. For example, page 3, line 14 states that Heiden et al. found that "mainly SQT" was induced by ozone but Heiden et al. says tobacco plants increased their SQT emissions while pine trees increased MT emissions. On page 3, line 29 the text states that Penuelas and Staudt report elevated SQT under ozone stress but Penuelas and Staudt only mention the sum of MT and SQT. The authors then go on to suggest that their finding that SQT responds to stress, while MT do not, fits with the literature but this does not seem to be the case. They also state that MT are not critical for oxidative stress (page 14, line 13) but I don't see this supported in the literature.

AC:Page 3 Line 14 (Page 7664. Line 15): We believe that we did not change the main result by Heiden et al.

The exact sentence is "while ozone may apparently induce biosynthesis and emission of volatile isoprenoids, mainly SQT, even in plants that do not naturally emit these compounds (Heiden et al., 1999)."was referring to tobacco plants. However, we will skip the "mainly SQT" to avoid confusions.

Page 3 line 29 (page 7665,Line 4): we rephrased the following sentence: "In their review, Peñuelas and Staudt (2010) reported a significant amount of results that indicate an elevated sum of SQT and MT emissions under ozone stress".

Page 14 line 13 (7679 Line 14): The sentence:" Since MT are not considered to be critical for oxidative stress, we assume that the high temperatures associated with high ozone are the main reason for this observed rise." will be rephrased at the revised manuscript as correctly pointed out by both referees #2 and #3and it will be replaced 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”

RC:The dynamic branch enclosure and the VOC analytical techniques employed by the authors are appropriate and they appear to be high quality measurements. I am concerned that they don’t have more frequent measurements of SQT speciation since this could have a major impact on their assumed flux given the very different O3+SQT reaction rates which could result in major errors in emissions given the large term to “correct” for O3+SQT losses. They state that the few measurements they do have suggest that SQT speciation doesn’t change but I am unconvinced since the existing literature suggests that we should expect to see changes in SQT speciation with different season and stress. At a minimum, I suggest including a sensitivity study where they assume some possible changes in the SQT speciation and show how this could influence the results. One ancillary measurement that appears to be missing is leaf terpenoid content which would have been a worthwhile addition.

AC:The referee correctly focuses on the derived k rate for the reaction of O3+SQT. We acknowledge the importance of this parameter and this is why we provided a very detailed explanation of how we derived the constant (which also comes in line with previously reported values; Page 7671, Line 5). The common problem of detecting SQT emission shows up: Either one quantifies highly time-resolved SQT emissions without ozone removal and individual SQT specification or one measures all the details of SQT emitted removing the ozone stress to prevent SQT oxidation during sampling with a minor time-resolution. Here we focused on not altering the ozone stress to investigate the impact on the emission pattern. Since SQT production is not a very rapid process and terpenes are stored in contrast to isoprene (see e.g. Guenther et al, (1995) formulations) the adaptation time requires a notable amount of time. However, the manuscript does not suggest that SQT species are similar along the season: Page 7670 lines 13-14. “but due the limited amount of samples analyzed, a clear conclusion about the relative abundances along the season cannot be driven.” Nevertheless the earlier work of Münz (2010) covering the late summer period agrees with the findings

of this study and suggests a similar emission split of SQT.

What the authors implied is that the impact on the reaction rate would not be as substantial as the referee claims to. This is the reason for the large uncertainty in this value. We included this in the earlier uncertainty investigations of the kSQT_O3 value. Nevertheless we appreciated his excellent idea about a sensitivity test. The results from the tests performed will be presented with the additional sentence:

Page 7671 Line 7: “Sensitivity tests on the ozonolysis rate constant did not show any substantial deviations on the calculated emissions. The upper and lower possible reaction rates would have resulted in a change on the measured emissions by only $\pm(17.3\pm6.1)$ ngg(dw)-1 h-1 on average.”

This clearly indicates the importance of the findings even without the continuous quantification of individual SQT emissions for the site of investigation. But certainly this point is the most critical.

RC:The major weakness of this study is that there are no replicates- they only made measurements on a single branch. The authors justify this by saying that “Bäck et al. (2012) found that in contrary with MT, SQT emissions do not defer significantly between the investigated coniferous trees (Scots Pine) and therefore smaller uncertainties would be induced when applying the algorithm”. This sentence is a bit unclear but it seems to say that we can trust this algorithm because Bäck et al. found little variation in SQT emission factors among different Scots Pine. However, the Bäck et al. result on emission factors is not very relevant for this study on emission response and may just say that SQT emissions from Scots Pine are not very important. What is relevant is that Heiden et al. found that Scots Pine exposed to ozone emit more MT but not more SQT. This suggests that there is considerable variability in SQT response to ozone among different species and does not rule out differences among individual spruce trees. I suggest two possibilities for making this manuscript acceptable for publication in Biogeosciences: 1) include some replicates (other individuals and species), or 2) remove the text on the quantitative algorithm and instead discuss how to go about making a quantitative algorithm and what would need to be done (i.e. more measurements) to do this.

AC:We understand referee's concern that the study includes results from a single branch but disagree with his interpretation of our statements regarding Bäck et al. (2012) and Heiden et al. (1999). However, the goal of the study was to conduct seasonal SQT emission measurements. This goes in line with the response to the former statement just made above. We could either observe the seasonality or switch among trees, since the discussed variability would have complicated the analysis. As correctly pointed out by anonymous referee #2, we provide a big dataset of SQT emissions, "considering how limited is the SQT emission dataset is worldwide". Nevertheless we agree on the need of further more diverse measurements of a single tree or even further trees. But the measurement technique is based essentially on the enclose approach. Applying more would be much more informative but out of our financial limit. BÓŞck et al (2011) reported similar composition of SQT among different trees of the same species at Hyytiälä field forest station. This study is of relevance to ours, since both studies are conducted in a coniferous type forest site originally managed by the forest agency. The essential point we wanted to make addresses the large variation found by Bäck et al. (2012) for MTs but much less for SQT. This might be an indication for the difference in production. For instance that MT production occurs much more flexible than SQTs. Nevertheless, we emphasize that her study was on Scots Pine and in any case stress the need for further measurements in order to confirm our observation in other ecosystems. The referee#3 is suggesting to either include further replicates or to remove the discussion. We believe that this study can stand alone since it considers 16200 emission data points with a deep and conclusive statistical analysis. Furthermore, we postulated a parameterization that describes in the best way the observations for the site of interest. Since we recognize the critical aspect of no continuous quantification of single SQT, we followed your valuable advice to perform sensitivity tests that revealed negligible deviations in the emission model. As we

stress out at the conclusions "more measurements are necessary in order to confirm the validly of this observation in other ecosystems". We would certainly be happy if further studies and groups would test these findings themselves. However, since the amount of SQT data presented in this study are sufficient and detailed statistical tests were applied in any aspect, we are confident in the findings presented. Therefore we are convinced that the publication of these results and discussions will give the opportunity to various groups worldwide to investigate the effect of ozone in SQT emission and broaden our knowledge on this very important atmospheric compound.

Specific comments:

RC:Page 9, line 22-23 (Page 7673 Line 12): The text says there are different beta values but they aren't statistically different Page 9, line 26 (Page 7673 Line 18): why should this influence SQT emissions?

AC:Indeed, the beta factor is inside the errorbars and the drought stress in this context cannot prove the observed differences in beta factors in the rounded digits provided. We might extend the digits further. But this won't lead to a very improved discussion. Therefore, we will rephrase the complete paragraph as following:

"On contrary, seasonal calculated β-factors showed similar behavior during the season. Slightly higher values observed during summer (βsummer = (0.12$\pm$0.02) °C-1), followed by autumn ones (βautumn = (0.11$\pm$0.02) °C-1). Temperature dependency found to be minimum during spring time (βspring = (0.09$\pm$0.01) °C-1), mainly because of the low β-factors observed during May (Fig. 2)"

RC:Page 11 and elsewhere: is the relative humidity correlation just due to temperature?

AC:Yes, we believe that RH is correlated with the emissions because of temperature issues (in low RH) and anticorrelates (in 100% RH) due to evapotranspiration issues. If one correlates the emission with water vapour mixing ratio or absolute humidity one finds a similar but reduced effect (about -0.1).

RC:Page 12, line 2-3(Page 7676 Line 17): the temperature is always below 30°C. Is this really a stress?

AC:The term “temperature stress” is not only apparent above 35°C or above. Depending on the plant or tree species this certainly causes stress even below 30°C. For spruce trees optimum temperature conditions are most likely below. At the site of interest the optimum might be somewhere between 15 and 18°C. One important point as well is the fact that the air temperature of 30°C is not defined as sunlit temperature but as the one in the shadow. Otherwise this would be a measure of solar radiation intensity. Therefore surface temperature can be notably enhanced because of albedo and the cooling intensity (evapotranspi-ration). Thus, it can be a stress depending on the plant species, especially for dark coloured coniferous ones. But in general the term “stress” is certainly a consequence of multiple environmental and biotic factors, not of temperature only.

RC:Page 12, line 10(Page 7676 Line 26): how does this explain the rise in basal rates?

AC:We observed higher emission rates at lower RHs (Fig 1d). As the reviewer correctly pointed out previously this might be caused by the temperature and the heating up of the needles in the sunlight.

RC:Page 15, line 3(Page 7680 Line 9): clarify this sentence

AC:Probably the referee is referring to the following sentence: “Nevertheless, the involvement of plant volatiles in destroying ozone may have a significant impact on the interpretation of the role of such emissions (Jardine et al., 2011).” What we mean here is, as pointed out by Jardine et al. to which we refer in this context, i.e. that we need to understand the role of SQT emissions. If this compound is also emitted to protect the plant from elevated ozone concentrations, then we need to take this into account when trying to interpret the measurements.

RC:Page 17, line 7: since you didn’t measure production rates or even pool size then how do you know this?

AC:We did not measure production rates or even pool size. However, after a rough calculation (F. Loreto; personal communication) and using literature values for stomata conductance we did not find any SQT pools inside the leaves.

We appreciate all the critical comments of reviewer #3 and thank him for his careful work that helped us to improve the quality of the manuscript.

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