MS No.: acp-2014-208, Biotic stress: a significant contributor to organic aerosol in Europe?

By R. Bergström et al.

Final response to the comments of referee #2:

We thank the reviewer #2 for the helpful comments. As a general remark: we do not intend to provide an exact answer how important biotic stress is for organic aerosol formation in Europe but to stimulate debate and further research.

Reviewer #2

The paper discusses an important issue of stress induced BVOC emission and the secondary aerosol formation. Although speculative, I feel that the paper is a valuable contribution and could be published after a few comments given below are satisfactorily addressed.
The authors assign only sesquiterpene and methyl salicylate to stress induced emissions. How about an increase in monoterpene emissions due to stress? E.g. mechanical wounding is known to increase monoterpene emissions from plants (e.g. Juuti et al., 1990). How would this affect the results?

Our response: referee # 2 is correct; monoterpene (MT) emissions are also often increased as a consequence of plant stress and this effect is not covered by our procedure of using emission patterns to relate stress induced emissions (SIE, here sesquiterpenes, MeSA, and C_{17} BVOC) to the MT emissions. By doing so we arbitrarily assigned all MT emissions to constitutive emissions. This was done because the MT emissions measured during our experiments were quite similar to those measured for unstressed plants of the same species.

Although there were no obvious indications of this, we cannot exclude that also the MT emissions from the investigated plants were increased due to the stress. However, this does not affect our main intention to stimulate research on (biotic) SIE, because SIE very likely contribute significantly to SOA. Independent of the situation during our measurements, neglecting stress induced MT emissions leads to an underestimation of the role of biotic stress to plants for their BVOC emissions and SOA formation: If also MT emissions would have been increased by stress during our measurements, the ratios SIE/MT emissions as used for modelling would have been too low. Using too low ratios would have led to underestimation of the role of the considered SIE for particle formation.

If, as we assumed, MT emissions were mainly constitutive, our procedure of using ratios would give a reasonable approximation for the role of the considered SIE. But again, the role of biotic stress for the SOA formation potential of all BVOC emissions may be underestimated because stress induced MT emissions are neglected.

As the main result of our modeling studies we found that impacts of biotic stress may be very high and stress induced emissions might contribute between 50% and 70 % to SOA mass formation. Given the known uncertainties, our estimate is already somewhat speculative and we do not want to add more speculation on this. We therefore refrain from including also stress induced MT emissions in our modeling studies.

We added the following sentences to Section 2.2:

Monoterpene emissions are also often increased due to plant stress (especially as a consequence of mechanical wounding; Juuti et al., 1990, Schade and Goldstein, 2003, Hase et al., 2011, Kaser et al., 2013). However, in this study all MT emissions were assigned to the constitutive emissions. This was made because the MT emissions measured during the JPAC experiments were quite similar to those measured for unstressed plants of the same species.

Reviewer #2:
The authors state that the stress-induced emissions are neglected in emissions models. However, as the basal emission factors (BER) used in the models are typically derived from published results on filed emission measurements by chambers or micrometeorological methods. In most cases no indication on whether the plant was biotically stressed or not was given. So it is likely that part of these measurements, and thus the BER derived from them, actually does include stress-induced emission.
This is even more likely for the emission factors derived from micrometeorological measurements, as any forest stand is likely to be under some level of biotic stress at any given time. This should be discussed in the paper.

Our response: this is a good comment; some of the SIE may be covered by field experiments. However, except for a few studies (e.g. Karl et al., 2008; Rice et al., 2008; Amin et al., 2012), field measurements were typically not performed on purpose in areas where forests are severely affected. Most such studies (e.g. Schade and Goldstein, 2003; Haase et al., 2011; Kaser et al., 2013) deal with abiotic, mechanical stress that according to our findings does not induce

sesquiterpene and MeSA emissions. SIE from severe infestations therefore should not often have been measured during field measurements.

We based our modelling on data given by Fischer et al. (2012) who find a certain degree of infestation for 10 – 25 % of the forest area. The source of SIE therefore is inhomogeneous and an important precondition to estimate emission fluxes of highly reactive sesquiterpenes in a reliable way (homogeneity of sources) is often not fulfilled. Nevertheless, as mentioned by referee #2, plants in all areas of the world are under some level of biotic stress. This may indeed occasionally lead to measurable amounts of SIE, e.g. SQT, even in areas with only moderate biotic stress. We considered that fact by assuming sesquiterpene emissions of 5% relative to MT to be covered by field measurements and included these in the base case 0.

In the following we perform a simple calculation showing the importance of SIE based on Guenther et al.: Guenther et al. (2012) estimate global, annual monoterpene emissions to ~160 Tg and global, annual sesquiterpene emissions to ~ 30 Tg. Applying a yield of 4 – 6 % for monoterpenes results in a global, annual SOA formation potential of 6.5 – 10 Tg·a^{-1}. Applying a yield of 17 % for the sesquiterpenes (Mentel et al., 2013) results in a global, annual SOA formation potential of ~ 5 Tg·a^{-1}. According to our results from measurements with living plants (Kleist et al., 2012, Mentel et al., 2013) sesquiterpene emissions are mostly induced by biotic stress. Hence, sesquiterpenes covered during field measurements at most probably low stress conditions, already significantly contribute to SOA formation. Furthermore, emissions of phenolic BVOC and C_{17} BVOC are still not included in modelling. Considering also such non-sesquiterpene SIE in modelling should give an even higher number for the global, annual SOA formation potential of SIE.

We will add the following text to Case 0 in Section 2.5:

The addition of 5% SQT is based on observations at the JPAC for experiments with no observable biotic stress (e.g. Mentel et al. 2009). Since SQT emissions are mostly induced by biotic stress (Kleist et al., 2012, Mentel et al., 2013) the 5% SQT emissions used in Case 0 can be considered as covering a low "background" biotic stress situation.

Reviewer #2:
The modeled night-time NO3 concentrations at Hyytiälä site seem very high. Rinne et al. (2012) reported the measured NO3 concentrations during summertime being below their detection limit of 1 pptv, whereas in Fig. 6 the concentration is more than order of magnitude higher. How well your

model compare with measurements e.g. for other oxidants (OH, O3)? How does this affect your results?

As noted by the referee, Rinne et al. (2012) found levels of NO_3 to be less than 1 ppt, whereas our model results suggest nighttime levels of 20 ppt. However, Rinne's data were from a tower located at canopy height, and just 10m from trees. NO_3 is known to have very large vertical gradients that call for great caution in the interpretation of canopy-level data. We are not aware of vertical measurements of NO_3 above European forests, but data from North American studies frequently show very low levels of NO_3 at ground-level and much higher levels aloft - 10s or even 100s ppt NO_3 (e.g. Brown & Stutz, 2012 and refs within). 1-D model calculations over Swedish forests also support very large gradients in NO_3 in the lowest 100s of metres (Johansson and Janson, 1993).

A secondary problem which would lead the model to overestimate NO_3 is our assumption of oxidant neutrality in which NO_3 is not consumed in NO_3 + BVOC reactions, except for isoprene. As explained in Sect.2.4, this assumption was necessary because we do not have chemical mechanisms to track the fate of BVOC oxidation products. In order to test the impact of this assumption we have re-run the model assuming full NO_3 loss upon BVOC reaction. The NO_3 concentrations were dramatically reduced, but the impact on SIE-SOA formation was just 30%, well within the uncertainties of this kind of study.

Evaluation of OH concentrations is also problematic. We are not aware of any direct evaluations of OH from regional CTM models in Europe. Box or 1-D model studies of forest-canopies are broadly consistent with measured OH or OH-reactivity, but with missing OH sinks (e.g. Mogensen et al 2011). Away from the canopy OH should be constrained by reasonably well known sources (ozone photolysis) and sinks (CO, CH_4, and many anthropogenic as well as biogenic VOC). For the west coast of Norway, Karl et al. (2014) found that the EMEP model gave 24h OH concentrations of 2.6×10^6 molecules/cm^3, in good agreement with previous calculations with another model (COSMO/MUSCAT). Box-model studies have also demonstrated that the basic EMEP gas-phase chemical mechanism provides results for OH and NO_3 which are in line with those of other (and more complex) models (Andersson-Sköld and Simpson,1999, Kuhn et al.1998).

Finally, for ozone, the EMEP model's predictions of ozone have been extensively evaluated over many years, and shown to compare favourably with measured values across a wide range of

sites (e.g., Jonson et al., 2006; Sakalli and Simpson, 2012; Gauss et al., 2014). Model performance for daily maximum ozone is much better than for daily mean ozone, mainly due to the difficulty of reproducing night-time ozone correctly. For example, in the latest evaluation the bias in daily mean ozone was found to be +10%, but just +3% for daily maximum ozone (Gauss et al., 2014).

To avoid lengthy discussions of the above which would unbalance the manuscript, we have added very terse summaries. In Sect. 3.3, we add a new paragraph:

The model calculated NO_3 concentrations are very high compared to the sub-ppt levels reported by Rinne et al., 2012 at canopy-height for Hyytiälä. However, aloft levels of NO_3 are often observed or calculated to be far higher than ground-level data (Brown and Stutz, 2012; Johansson and Janson, 1993), so our values may be reasonable. In any case, model calculations where we relax our oxidant-neutrality assumption (Sect. 2.4) and allow 100% loss of NO_3 have shown that even though NO_3 levels are reduced dramatically, the effect on SIE-SOA is moderate, about 30%.

For the ozone and OH issues, we have simply added further citations and a few words in Sect. 2.4:

For short-lived radicals, evaluation against measurements is problematic for regional scale CTMs. The EMEP MSC-W chemical mechanism has been shown to provide results for OH and NO_3 in line with other (more detailed) models (Andersson-Sköld and Simpson, 1999; Kuhn et al.1998; Karl et al., 2014). Model results for NO_3 are discussed further in Sect. 3.3.
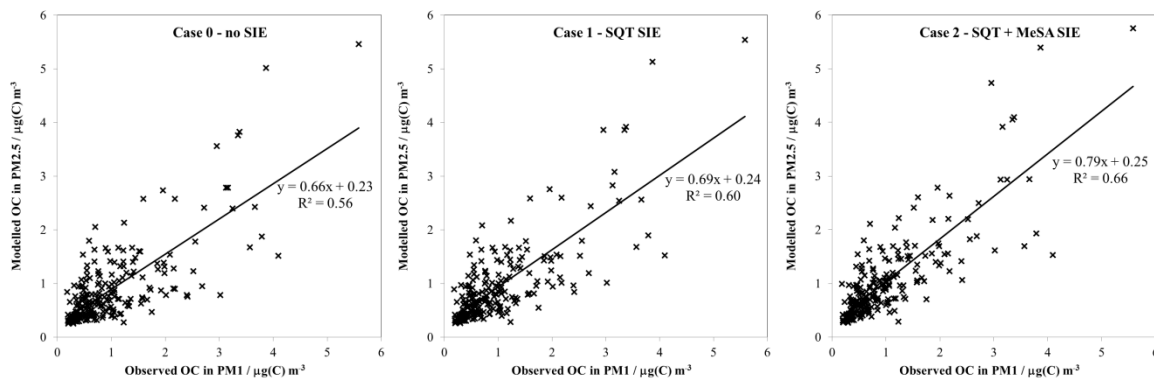
Technical comments

The text within the Fig. 1 is very small. Could it be made a bit larger.

Done

Could you add model-measurement correlation plots as panels in Fig. 2.

Done

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