

***Final response to Atmos. Chem. Phys. Discuss., 13, 7463-7502, 2013,
Mentel et al.: Secondary aerosol formation from stress-induced biogenic
emissions and possible climate feedbacks***

We appreciate the reviewer's efforts and helpful comments. All remarks were considered and we feel that the corresponding changes improved our manuscript. To allow easy discrimination between the reviewer's remarks and our responses, the remarks are set in bold and our responses are written in italic. When citing the manuscript, old text is written in black letters, new text is written in red letters. In the new version of the manuscript changes are highlighted.

Reviewer #1:

The abstract would benefit from some quantitative information on the findings together with an uncertainty discussion.

We added quantitative information in the abstract. The respective lines now read:

“Sesquiterpenes, methyl salicylate, and C₁₇-BVOC increase SOA yields. Mixtures including these compounds exhibit yields between 17 and 33 %, significantly higher than mixtures containing mainly monoterpenes (4-6% yield). Green leaf volatiles suppress SOA formation, presumably by scavenging OH, similar to isoprene.”

The limitation of this paper is the restricted number of investigated experiments in terms of stress origin and of plant types, which is however fully justified by the difficulty in performing such experiments. This prohibits an accurate extrapolation of the presented results to global scale. This limitation has to be emphasized in the discussion of the implications of the findings in section 4.

Indeed, accurate extrapolation is limited by the restricted number of experiments and in particular, the so far missing possibility to normalize degrees of biotic stresses. Our goal is to initialize discussions about the potential importance of SIE for SOA formation and couplings to climate change. For that purpose we had to make some generalizations. However, we did not claim to quantitatively extrapolate the data. To emphasize this we changed the manuscript accordingly (see next point).

A few additional changes could further improve the readability of this very good paper. Section 4.1 should be broken in two sections. The first section will present the BVOC emissions and SOA formation results as deduced from the experiments presented in this study and will contain the first part of the actual section 4.1. The second section will be on the 'Implications of the finding for climate impact of BVOC/SOA' and will contain the last part of the actual section that is more speculative as is also the case of the actual section 4.2.

Overall Section 4 needs to clearly refer to the limitation of the study in representativeness due to the limited number of experiments as above mentioned.

We followed the reviewer's suggestion and divided section 4.1 and added a new section 4.2 entitled "Impacts of SIE on SOA formation and climate". We furthermore changed the header of the former section 4.2 (now 4.3) from "Climate change and SIE SOA" to "Examples for possible feedback effects via SIE-SOA" in order to highlight the exemplary character of this section. The section was shortened; only two possible scenarios are shown in the new Fig. 9 now; the complexity of the system was pointed out more clearly. We acknowledged that there is no possibility at the moment for qualitative or quantitative upscaling (in the new Section 4.3).

page 7464, line 16: replace 'propose' by 'discuss'.

Done

page 7476, lines 17-20: I will agree with this statement for present climate but insects might be different in a future climate. So some rephrasing is needed here.

In these lines we substantiate why we at all treat C₁₇-BVOC as stress-induced BVOC. C₁₇-BVOC was observed for a coupled plant-insect system and details could not be separated. We do not intend to make statements about development of plant-insect interactions and related emissions of C₁₇-BVOC in a future climate. However, we believe that the assignment of C₁₇-BVOC as stress induced emission is correct. No changes made.

page 7476, lines 27-28: several references are given. it would be good to provide some insight on the content (of interest) of these studies.

We added some words with this respect. The new text now reads:

"Emissions of MeSa and SQT are not specific for the plant species and stress conditions investigated here. Phenolic BVOC (with MeSa being predominant) originate from the phenylpropanoid pathway (Colquhoun et al. 2010) and the activity of this pathway is induced in particular by pathogen attack (e.g. Jansen et al., 2011 and references cited therein). Emissions of MeSa and SQT during insect infestation were also reported for Eurasian (Kleist et al., 2012) and for a North-American conifer species (Joó et al., 2011). Therefore the importance of our SIE-SOA yields may apply to a wider range of situations and regions despite the limited number of experiments presented here."

For better understanding we added the reference Jansen et al., 2011. Because some remarks on literature data regarding the C₁₇-BVOC were already given some lines before the new text passage, the citation "Nazzi et al." was deleted in the new text passage.

page 7477, lines 15-18: this information should come earlier in the discussion of the results.

We agree that our notations of “yields” was somewhat insufficiently explained and possibly at the wrong spot. We therefore deepened the description of our mass yield determination in the experimental section in favour of the last paragraph of introduction, which was cancelled:

“The BSOA yields were determined as established in detail in Mentel et al. (2009). By changing the conditions in the plant chamber the concentration of BVOC in the reaction chamber was varied. The formation of BSOA mass was determined as function of the BVOC mass that reacted with OH and O₃. We observed linear relations between BSOA formation and BVOC consumption in the applied concentration range (see later Figures 2, 3, 5, and 7). Under these conditions the slope obtained by regression analysis is defined as the incremental mass yield. The incremental mass yield quantifies the efficiency to convert BVOC mass by gas-phase oxidation into particulate matter (BSOA). The incremental mass *yield* is independent of the amount of consumed BVOC for the conditions here, but the actual obtained BSOA *mass* is of course proportional to the amount of BVOC, which is available and is consumed. However, the incremental mass yield may depend on the emission pattern because different BVOC can exhibit different incremental yields.”

page 7466, lines 1-2: this sentence needs a second part, which briefly mentions (here) what else is needed.

The sentence was complemented by the following:

“Our recent experiments suggest that it may not be sufficient to consider only isoprene and monoterpenes and BSOA originating from those compounds in future (and current) climate scenarios. In addition stress induced BVOC emissions as well as climate change induced impacts on BVOC emissions (Kleist et al., 2012) should be considered.”

page 7466, lines 24-25: some information on NO_x levels in the chamber has to be provided.

The required information was already included (former p. 7470, last line). In addition we added “[NO_x] < 300 ppt” in the “Experimental” section.

page 7466, line 11: phenolic BVOC: Guenther et al (2012) indicate toluene (that is an aromatic hydrocarbon but not a phenol) as one of the 15 identified stress VOCs. Please rephrase.

We indeed mean phenolic BVOC and not aromatic BVOC in general. To clarify this we deleted the citation “Guenther et al., 2012” and added the following definition (former p. 7466, lines 9 ff):

“They consist of different BVOC classes such as BVOC synthesised within the phenylpropanoid pathway (e.g. Colquhoun et al., 2010, here denoted by “phenolic BVOC”), BVOC synthesised within the octadecanoid pathway (here denoted by “green leaf volatiles”, GLV, e.g. Croft et al), and sesquiterpenes (SQT).”

Aromatic molecules as benzene or toluene are not produced within the phenylpropanoid pathway (see Heiden et al., Toluene emissions from plants. Geophys. Res. Lett. 26, 1283-1286, 1999). We hope that the reference to the phenylpropanoid pathway avoids misunderstandings.

page 7467, lines 24-27: How the chamber was cleaned between two experiments?

The reaction chamber was not cleaned in the classical sense, since it is permanently connected to and flushed by plant chamber flow and the conditioning flow. The chemistry is controlled by switching the UV light on and thus OH for 6-8h and off again. We added the following text to chapter "Experimental":

"After changing the conditions in the plant chamber we allocated 8 h for establishing new steady state conditions in the reaction chamber before the next experiment. Particle formation was studied once a day with time intervals longer than 12 h with UV off between two particle events. In these periods the reaction chamber was flushed and conditioned by the plant chamber flow and the conditioning flow, both of 16 l min^{-1} and particle free. Since the residence time in the reaction chamber is about 45 min we thus allowed more than 10 e-folding times to remove the reaction mix from the previous experiment including particles and to re-condition the chamber."

page 7468, lines 21-26: Did the conditions of experiment #1 detailed here have been reproduced in the control experiment?

In control experiments we determined the incremental yield of individual BVOC using an artificial diffusion source without the plant chamber. The conditions in the reaction chamber were reproduced and kept the same as in the experiments with plants. For clarification the following sentence was added:

"Conditions in the reaction chamber were kept identical to those of the experiments with the plants."

page 7468, last line : an extra parenthesis has to be removed.

Done.

page 7477, line 24: itself has

Was changed to "GLV themselves have...".

page 7479, line 9: Tsigaridis

Thanks for helping us avoiding an embarrassment. Done

page 7479: last 2 lines: Several papers before the Spracklen et al 2011 study mentioned the possible anthropogenic enhancement of biogenic SOA production (e.g. - prior 2011 and in increasing year order- Kanakidou et al J. Geophys. Res., 105,9243-9254, 2000; Tsigaridis and Kanakidou, Atmos. Environ., 41, 4682–4692, 2007; Weber, R. J., et al., J. Geophys. Res., 112, D13302, doi:10.1029/2007JD008408, 2007; Clarton et al Environ. Sci. Technol. 44, 3376–3380, 2010).

Thanks, the necessary citations are included now.

Figure 6: a parenthesis is missing in the legend (SQT).

Parenthesis is added.