**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "The chemical and microphysical properties of secondary organic aerosols from Holm Oak emissions" *by* N. Lang-Yona et al.

N. Lang-Yona et al.

t.mentel@fz-juelich.de

Received and published: 12 July 2010

Reply to Anonymous Referee #2 Received and published: 13 April 2010

Comment: In this research, the formation and properties of secondary organic aerosols (SOA) from Holm oak emissions were studied using a biogenic aerosol environmental chamber. Holm oak was used as a model plant for the Mediterranean area. The temperature in the chamber was varied in order to study temperature dependence of volatile organic compound (VOC) emissions and subsequent SOA formation (i.e. to simulate future warmer climate). Furthermore, chemical and physical properties of SOA particles (e.g. hygroscopicity and optical properties) were characterized to

evaluate impact of formed SOA on the climate. Generally, the area of this study is very interesting since biogenic SOA particles are suggested to have an important impact on the global climate. Furthermore, there are still not many studies on SOA formation in which living plants have been used as natural sources of VOCs. Therefore, this study presents novel and important results on SOA formation from Holm oak emissions. The manuscript (MS) is quite well written and clear and the scope of MS is suitable for publication in this journal. However, there are some minor comments and suggestions that should be considered before publication.

Reply: We thank the Reviewer for the assessment of the paper and the constructive comments. Each of the points was considered and addressed as outlined below. The position of modifications relates to the new, revised pdf-document.

Comment: 1) Abstract. There is mentioned that Mediterranean areas may have a stronger impact on VOC emissions and SOA formation than in areas with Boreal forests. I think that is too strong a statement based on results reported in this MS. For instance, the materials of this study are very limited to make this kind of statements, only a few experiments were carried out mainly with one tree species (Holm oak). I think that more experiments with different kind of species in different conditions (temperature, light, seasons, drought, and other abiotic and biotic stresses) as well as large scale climate modeling studies are needed for the complete comparison between Mediterranean and Boreal areas. The main results should be presented in the abstract.

Reply: We present now more material in a supplement. For the Mediterranean trees experiment we have applied high temperatures in ranges which are relevant to the region. Under these elevated temperatures enhanced MT emissions were observed and this has been published before (Staudt and Bertin, 1998). A substantial enhancement of monoterpene emissions in the Holm oak experiments was measured and we have clearly observed more SOA formation. The reviewer is correct noting that besides temperature and light intensity there are other factors that determine emissions of VOC by plants. However to determine all the impacts of these factors on SOA formation would

certainly go beyond the scope of this work. We therefore restricted our conclusion to the impact of temperature. To make this point clearer we changed the text, accordingly.

Based on the Reviewer comment, we toned down the statement in the Abstract and in the Conclusions. Supported by the new data, the statement in the Abstract reads now (p. 2, line 2ff): "The increase of Holm oak emissions with temperature ($\approx$ 20 % per degree) was stronger than e.g. for Boreal tree species ($\approx$ 10 % per degree). The SOA yield for Mediterranean trees determined here is similar as for Boreal trees. Increasing mean temperature in Mediterranean areas could thus have a stronger impact on BVOC emissions and SOA formation than in areas with Boreal forests."

In the Conclusion section (p.17, line 3ff): "The increase of Holm oak emissions with temperature (20% per degree, see supplementary material and Staudt and Bertin, 1998) was stronger than that described for Boreal tree species (ca. 10% per degree, e.g. Guenther et al., 1993, Guenther et al., 1995, Janson et al., 1993, Shao et. al., 2001). The incremental yield of 6% for SOA formation found for monoterpenes from Mediterranean species is nearly the same as for Boreal species (5.7%, Mentel et al., 2009), independent on the BVOC patterns or the detailed reaction conditions. Therefore, assuming the same atmospheric conditions for particle formation and neglecting stress impacts on the plants' BVOC emissions, a similar temperature increase for Holm oak and a Boreal species would cause different increases in particle formation. For example a 2 degree increase would result in a 50% SOA mass increase for Holm Oak caused by the high temperature dependence of ocimene emissions. For Boreal forest trees the increase would be only 20%. Volatility measurements show that the volume of SOA decreases by only 20% per 50 degree change in temperature (Jonsson et al., 2007), suggesting that the SOA increase due to increased emission would be the dominant effect under the projected climate change. However, this supposition awaits further experiments and modeling efforts considering also changes of the boundary conditions."

Comment: 2) Introduction. There are quite many references on general aerosol/climate

effects in the first chapter. I think that only the most important are needed.

Reply: We removed 4 references from the first paragraph of the introduction section. However, to give a potential reader of our manuscript the best possible overview regarding aerosol climate effects we prefer to keep all other references in the reference list.

Comment: 3) Methods. a) For clarification, a table which summaries the conducted experiments (date/ID, plants, number of plants, VOC-induced/Ox.-induced, temperature, light, RH, total VOC concentrations, etc.) should be included in the Methods chapter.

Reply: We added a new Table 1 with the experimental conditions.

Comment: b) 1st chapter (p. 4757, l. 11): Is there one comma missing (before 3 Aleppo Pine)?

Reply: comma added.

Comment: c) 2nd chapter (p. 4757, l. 19): I think that "the average residence time" is more informative than "the residence time". Reply: changed accordingly

Comment: d) p. 4761, l. 5: acronym DMA not described. Reply: acronym DMA explained.

Comment: e) Same chapter. What was residence time from aerosol humidification to particle classification in HTDMA system? And is this enough long to achieve complete water uptake for SOA particles at certain RH?

Reply: In our setup the particles are pre-humidified in a Nafion tube. The pre-humidfied aerosol enters a cooled section (20°C), which brings RH to its final value. The aerosols remain in this humdification section for approximately 30 s. In the DMA the particles are in contact with the sheath air which was humidified to the same RH value. The RH is constantly monitored. We are confident that our method guarantees long enough contact time to complete water uptake.

We added a sentence on the contact time for particles with the final humidity (p. 9, line 3ff).

"The particles remained for approximately 20 s in contact with the selected humidity before they enter the SMPS which operated with sheath air of the same humidity."

Comment: 4) Results and discussion. a) Eq. (1) (p. 4763, l. 3): Although PPFD has been described earlier, it should be also done after this equation.

Reply: Thanks for the comment, done.

Comment: b) Ch. 3.2 (p. 4764, l. 5-): It is mentioned in the text that flush out (dilution of chamber air) decreases the particle concentrations. Can you estimate the effect of other losses on particle concentration (e.g. wall losses due to diffusion, sedimentation, etc.)? Furthermore, VOC from plants were introduced to chamber during experiments. How does it affect particle concentrations (flush out reduces particle concentrations but this may increase VOC concentrations and SOA formation in the chamber).

Reply: Our setup is operated as a continuously stirred tank reactor (CSTR) and we transfer BVOC in a steady stream from the plant chamber to the reaction chamber. To that we add the flows for ozone and humid air which contribute 50% to the total flow. All flows are kept constant and the total flow determined the residence time in the reaction chamber. For the gas-phase part we operate on steady state conditions (with short transient periods when the UV light is switched on) for the BVOC reactants, oxidants, and reaction products. This was described in detail in Mentel et al. 2009. Also the aerosols are flushed out by the same process but this cannot affect the BVOC concentrations in the reaction chamber. By operation as CSTR the entire volume is mixed wherein the particles are formed. The effective mixing bares the risk of diffusional wall losses and sedimentation. Such possible losses were estimated from the decay of particle mass with time after the OH oxidation was stopped. The decay times measured for particle mass loss were quite similar to the residence time of the air in the reaction chamber and from this we conclude that, on the time scale of our observation,

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losses by sedimentation are negligible compared to the losses caused by the outflow. We now give a short note in the text (p.11, line 25), however, we refrain from explicitly describing this point because this would take much more additional information making the present manuscript much too long. "Other particle losses were negligible as the lifetime of the particle volume after stopping the chemical production is quite the same as the average residence time in the reaction chamber."

Comment: c) Ch. 3.4.1 (p.4767, l. 4-): Can you compare GF results to other chamber and field results (e.g. from a-pinene chamber studies).

Reply: We added a comparison to other chamber and field results (p. 14, line 15ff): "The observed values are comparable with measurements of Varutbangkul et al. (2006) who observed GF(85%) in a range of 1.06 - 1.1 for SOA from several monoterpenes. Good et al. (2010) report GF(90%) for SOA generated from pure α-pinene. At 90 ppbC initial concentration. GF(90%) increased from 1.1 to 1.2 (HMAN instrument) during the period 2 - 8 h after particle generation. If 370 ppC α-pinene was used initially the GF(90%) were lower and raised from 1.06 to 1.12 (Good et al., 2010). In their review Swietlicki et al. (2008) summarize GF(90%) for field studies in rural areas. Our GF(90%) is at the low end of their less hygroscopic group (LH). Similar values were observed at many locations, e.g. in the Po-Valley at San Pietro Capodifiume (1.10 for 150 nm particles)."

Comment: d) Ch. 3.4.1 (p.4767, l. 16): Please define acronym SS in order to avoid misunderstandings.

Reply: acronym now defined at first use in paragraph.

Comment: 5) Summary and conclusions. a) p. 4769, l. 26-: Why ocimene emissions have a high temperature dependence?

Reply: This is indeed a very interesting question. However, at the moment this is just an observation as described in Staudt and Bertin (1998) and in the supplement added

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now. We have no answer yet.

Comment: b) p. 4770, l. 7: Please describe T-induced shifts.

Reply: We rephrased the whole paragraph and the sentence is now obsolete.

Comment: c) See also comments for Abstract (1).

Reply: see Reply to comment 1) abstract.

Comment: 6) Tables. Please add a table that summarizes experiment conducted (see comment 3a).

Reply: the Table 1 was added

Comment: 7) Figures. a) Fig. 2: Please include total VOC concentration values to this figure or an experiment summary table.

Reply: the total BVOC concentrations are now listed in new Table 1.

Comment: b) Fig. 4 and 5: Is there any specific reason to use different x-axis units?

Reply: In case of condensational growth rates we prefer to plot against BVOC mixing ratios in units of ppbC since the mixing ratio is commonly used in atmospheric chemistry. In case of particle mass we changed to mass concentrations for the BVOC as this enables the reader to directly assess the yield from the slope. We therefore left the different units. However, mixing ratio and mass concentrations are both given in the new Table 1.

Comment: c) Fig. 6. The figure will be easier to read if colors are described as pure hydrocarbons, singly oxygenated and multiply oxygenated (not only CxHy, etc.).

Reply: We prefer to leave figure 6 as it is, but explained now CxHy etc. in the way proposed by the reviewer, in the figure caption.

Comment: d) Fig. 9. Both situations can be plotted in one plot (two separate plots are not needed).

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Reply: Done

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 4753, 2010.