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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

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Reply to Anonymous Referee #1 Received and published: 9 April 2010

Comment: This is a neat study that examined the effect of three different temperatures (25, 30 and 35_C) on the emission of volatile organic compounds (VOC) from Mediterranean Holm Oak, and the impact this had on the formation of secondary organic aerosol. The work was carried out in the laboratory based plant-aerosol chamber facility at Julich. The temperatures used are suitable and relevant to a Mediterranean tree species. The use of real plant emissions also ensures atmospherically relevant concentrations of VOC were studied. In addition to altering the temperature, two aerosol

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chamber filling procedures were used to optimise particle growth based on maximising or minimising the presence of OH at the time of flushing with plant chamber air. The paper does address a relevant scientific question – that of SOA formation under changing temperature and the methods are clearly outlined with only a few minor omissions. The abstract needs a little work but, the overall presentation is good and there are no extraneous figures or tables.

Reply: We thank the Reviewer for the through and constructive review of our paper. We have seriously considered all points raised by the referee and modified the paper accordingly. Our reply is given following each comment. The position of modifications relates to the new, revised pdf-document.

Comment: 1.) The abstract (line 6) mentions the investigation of varying light intensity as well as temperature. This is referred to again in the results section, (paragraph two of section 3.1 Plant emission patterns of volatile organic compounds). However, these data regarding effect of increasing light intensity on VOC emissions and subsequent SOA formation are not included. Given that the experiments presented in the manuscript are not replicated sufficient times for a biological system, I would like to see this data to: 1. demonstrate that the VOC emissions at a constant temperature and at the light intensity selected for use in the final experiments were not significantly varying with time, and 2. support the statement that "the emission behaviour was typical for Holm Oak" (final paragraph, section 3.1).

Reply: The Reviewer has raised important points related to the applicability of the plant chamber setup, as well as to the characterization of the plant emissions and the sensitivity of the SOA yield and microphysical properties to the detailed composition of the VOC mix. We note that Mentel et al (2009) have already demonstrated the applicability and relevance of such experiments to atmospheric processes, such as in the boreal forest atmosphere. This was done by discussion of the aerosol formation yields and the comparison with observations reported by Tunved et al. (Tellus, 2008). We have also shown that the aerosol yields and the microphysical properties are invariant of

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the details of the BVOC mix in the chamber. Therefore, our studies suggest that the biological reproducibility is not the central issue of SOA formation and microphysical properties. Moreover, we determined the emission strength and the emission patterns in all cases (Figure 2). As the title of this paper suggests, microphysical properties of the formed SOA aerosols are the goal of this study and the plants are used here as a source for complex and realistic source of VOC for the formation of the aerosols. Having said that, we keep in mind that this is a model system and a process study that by definition reduces the atmospheric complexity to the conditions employed in the experiment. Furthermore, we also agree that understanding the plants' behavior is important, as the Reviewer correctly remarks, but this is not the goal of this paper.

The Reviewer questions the dependence of the emissions on light and temperature. These are important points that need indeed more clarification. Given the length of the paper and its scope, we did not think it fit to include this kind of data in the original submission. However, we appreciate the comment and have added supplementary material that discusses our studies which have confirmed exactly these points. The enclosed supplement identifies and confirms several important topics as outlined below (taken from the summary of the supplementary material):

a) The results indicate that a part of the monoterpene emissions from Holm oak, Palestine oak and Aleppo pine can be parameterized using phenomenological algorithms (named as Group 1 monoterpenes in the supplement). That suggests that the emissions are stable and predictable under our operating conditions. Ocimene emissions are exceptional, however. Ocimene emissions were more variable, although temperature and PPFD were constant. As a result, it was impossible to apply the usual phenomenological algorithms. Nevertheless, Ocimene emissions were strongly dependent on both, temperature and light intensity. This behavior has been observed before by other groups and in particular the extreme dependence of Ocimene emissions on temperature was extensively described in Staudt and Bertin (1998). b) Identical to the findings described by Staudt and Bertin (1998) we observed that Ocimene emissions

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have high temperature dependence. Caused by the lower temperature dependence of Group 1 monoterpene emissions, a change of temperature changed the emission pattern; Ocimenes emissions are favoured at higher temperatures, and vice versa. This was observed for all plant species investigated here and also for the Quercus ilex plant used to determine microphysical properties of secondary organic aerosols. The behavior of the latter may therefore represent the broad spread Mediterranean species investigated. c) Temperature coefficients determined for the Group 1 monoterpene emissions are high. Compared to the temperature coefficient recommended for Boreal species (e.g. 9 % per degree, Guenther et al. 1993; Guenther, 1997; 13 % per degree, Shao et al. 2001) they are up to a factor of 2 higher (See Table S3). Hence, temperature increase might have stronger impacts on monoterpene emissions in the Mediterranean region than in the Boreal regions. This effect is synergistically enhanced by the strong increases of Ocimene emissions with temperature. 1) As shown by Mentel et al. (2009), the incremental yield of SOA formation from monoterpenes is to a good approximation independent of the detailed emission pattern. Thus, at otherwise unchanged conditions, the stronger increases of monoterpene emissions from Mediterranean species would be followed by stronger SOA formation compared to the increases in regions with Boreal forests.

The abstract was modified accordingly. We refer now only to the temperature dependence, but gave the additional data for the small Mediterranean stand (see next comment) a larger weight (p. 1, line 15ff, p.2. line 2ff).

Comment: 2. Figures 4 and 5 appear to indicate that only one experiment at each temperature level was undertaken. I have a number of questions regarding these figures. Do the figures include both methods used to maximise SOA growth (Ox-induced and VOC induced)? If so it would be useful to indicate these points separately. Does it improve the error terms if one regression line is put through the Ox-induced method, and a second through the VOC-induced method? One experiment on the small Mediterranean stand is not enough to confirm that the emissions and subsequent SOA forma-

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tion were typical for this species. A minimum of three replicates are required for any biological system. Based on one experiment I am not confident of the comparison to the Holm Oak. Could confidence bands be shown for the regression line?

Reply: In Figure 2 we showed the seven measured BVOC patterns of the experiments that were used in Figure 4 and Figure 5, six data point for the oak and one data point for the Mediterranean stand. We now analyzed 4 more experiments with the small Mediterranean stand, thus we have 5 data points in total from the Mediterranean stand. The results were added to Figure 2, Figure 5 and Figure 6. The new figures 4 and 5 therefore contain 11 data points and Figure 2 contains the patterns of these 11 experiments. We furthermore added a new Table 1 with the experimental conditions. From this new Table 1 it will also be clear that data points were repeated at the same temperature in the plant chamber. Please note that the x-axes of Figures 4 and 5 are not the temperatures of the plant chamber but the mass of the BVOC (Figure 4) respectively the carbon mixing ratio (Figure 5) introduced into the reaction chamber. Both are listed in Table 1 together with the temperature in the plant chamber in Table 1. The BVOC concentrations for the small Mediterranean stand were in a range 30 -190 ppbC (15-95 ug/m3). These data were included in the overall linear regressions for mass yield and condensational growth. The slope for mass yields increased from 0.057 to 0.06, the slope for the condensational growth rates remained unchanged, the intercepts changed somewhat within the errors. Error bars for concentration, mass, and growth rate are now shown in the Figures 4 and 5. Changes are marked in the figure captions and in the manuscript.

As stated in the manuscript, we optimized the setup in order to grow large particles for the characterization of microphysical properties, especially the optical measurements. To prevent unwanted nucleation due to ozonolysis without OH, the UV light in the reaction chamber was switched on before the visible light in the plant chamber. This implies that OH radicals were already present in the reaction chamber. For that reason we have 4 experiments with VOC induction and only 2 Ox.-induced experiments for the Oak. We

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have modified the Figures 4 and 5 and the Ox.-induced experiments for the Holm Oak are now marked with black squares in the new Figures 4 and 5. The Mediterranean stand experiments were all performed with ox.-induction, which is standard procedure as described in Mentel et al. 2009. If we separate the 4 VOC-induced experiments from the two ox.-induced points for the Oak and the 5 data points for Mediterranean stand experiment, we obtain SOA yields (slopes) of 4.4%+/-1.2% for the VOC-induced and 7.0%+/-0.4% for the ox.-induced experiments, respectively. These are within the error limits of the reported common yield of 6.0 +/- 0.6%. Intercepts are zero (insignificant) within the error limits. The errors are not more constraint, but this due to the limited number of data points after the splitting.

The revised manuscript contains the new Table 1 and the modified graphs Figure 2, Figure 4 and Figure5.

Comment: 3. Section 3.2. The authors write that "the SOA formation potential of tree species just depends on the amount of emitted VOC, as long as the emissions mainly consist of monoterpenes". By this statement I believe the authors to mean that if you removed every other variable, affecting SOA formation not emitted directly by the tree species in question (for example, humidity, isoprene, oxidant levels, pre-existing seed and acidity of seed), the only direct influence on SOA formation is the amount and type of VOC emitted. However, this is a virtually impossible situation to find in nature as the authors note in their conclusions. They acknowledge the limitations of the chamber design in not being able to introduce pre-existing seed and mention the potential influence of isoprene on SOA formation. I believe that the authors' statement in section 3.2 is confusing and of low scientific value given the highly restricted limitations it implies. I feel this statement should be removed.

Reply: As shown in this paper and in Mentel et al (2009), the microphysical properties of the aerosol and their growth rate do not depend much on the exact species in the BVOC mix but on their total amount. Therefore, we argue that the statement is scientifically sound and we have not changed it. Because of the complexity of natural SOA

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formation, the approach we have taken is to isolate and understand sub-processes. It is of course very difficult to simulate nature in a plant chamber, and this is not what was claimed. In fact, as the reviewer noticed, the limitations of the study were clearly stated and discussed in this paper. This paper refers to the SOA formation potential from tree emissions. As we showed here and in previous papers this is easy to quantify for (basal) MT emissions, but more complex for ocimene. It is of course accepted that the atmospheric conditions can modify the formation of SOA from the same mix. For example, high isoprene concentrations suppress OH (Kiendler-Scharr, Nature 2009). Introducing pre-existing aerosols will not lead to substantial changes in the growth rate as can be conclude from the comparison with Tunved (2008). However, it is assuring that in the limits of biogenic emissions which are dominated by MT (which are often encountered in places such as the Boreal forest and perhaps also in the Mediterranean), this is a relatively simple situation to treat. We regard this as an important finding and implication of this study that can be tested in the future in models and observations. Given the light and temperature dependence data that we now have added, we believe that we have generated data that can be used in models. The reviewer is absolutely correct that much more work is needed, and different conditions must be studied. However, this extension is beyond the scope of this paper.

Comment: 4. Summary (section 4, line 21). The authors suggest that the values for SOA formation obtained from their experiments are relevant to the atmosphere and can be applied to model calculations. I disagree with this statement and suggest that the data can not be used in model calculations due to the absence of pre-existing seed which can have a significant impact on SOA yield and growth rates. I think this sentence should be revised or removed.

Reply: The Reviewer is correct that condensation on pre-existing aerosols can be significant under some atmospheric conditions. However, many types of aerosols exist in different environments (soot, sulphate, dust etc). For the presented initial experiments we decided to carry out experiments under clean conditions in which SOA formation is

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easier. As a matter of fact, as initial SOA particles form in the chamber, the growth can be described as growth on pre-existing (SOA)) particles. Under the conditions specified in the paper, all findings suggest that the growth is linear and can be extrapolated to atmospheric conditions as found for Boreal species (Mentel et al (2009)). If we accept that SOA may be a fraction of the pre-existing aerosol in forest environments, the process we observe in the chamber is representative. We agree with the reviewer that it may be a good idea to use other types of pre-existing aerosol in the chamber but as described above we chose to start with a simplified system.

The following explanation is now added to the paper (p.16, line 28ff) "The growth rates were determined after the initial aerosols nucleated. Therefore the linear growth observed in the chamber is conceptually similar to growth on pre-existing atmospheric aerosol. In addition since the SOA yield measured in the chamber matches yield observations in the Boreal environment (Mentel et al., 2009, Tunved et al., 2008) we suggest that the process we observe for the Mediterranean species is also representative and the values for aerosol yield are relevant to the atmosphere and could be applied to model calculations."

Comment: 5. Summary (section 4, line 24). The authors suggest their measurements show that the SOA formation for Mediterranean species increases more with increasing temperature than for Boreal species. However this is based on the false assumption that there are no stress induced changes in VOC emissions. There are numerous studies that show how VOC emissions change with differing environmental stresses (see for example isoprene emission increasing with ozone (Velikova et al, 2004) and high temperature (Sharkey and Yeh, 2001), drought effects on monoterpenes (Lavoir et al, 2009) and sesquiterpenes (Ormeno et al 2007). Furthermore, as well as being a stress compound, ocimene which the authors highlight, is strongly dependent on instantaneously fixed carbon from photosynthesis (e.g. Noe et al, 2006). Therefore, in the absence of other stresses (i.e. water limitation) which would close the stomata and significantly reduce carbon assimilation, the emission of this compound will

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increase with photosynthesis. The authors need to better support the conclusion that the increase in VOC emission (and therefore SOA formation) is higher for Mediterranean species than boreal species, given that the majority of this difference is based on ocimene emissions. This could be achieved by including gas-exchange data.

Reply: 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, as now described in the supplementary material and 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 the impacts of these stress 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.

Based on the Reviewer comment, we toned down the statement. We replaced the paragraph by the new paragraph (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

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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."

Minor corrections:

Comment: 1. I do not understand the sentence in the abstract “monoterpenes dominated the VOC emissions from Holm Oak and temperature increase enhanced the emission strength under variation of the emission pattern” What do you mean by “under variation of the emission pattern”? Please clarify.

Reply: The sentence has been changed to (p.1, line 20f): "Monoterpenes dominated the VOC emissions from Holm Oak (97.5%) and Mediterranean stand (97%). Higher temperatures enhanced the overall VOC emission but with different ratios of the emitted species."

Comment: 2. Introduction, line 15 “plants exposed to high pollution and CO2 levels will close their stomata:” Do the authors mean ozone when they say high pollution? If so, this is not always true. Low concentrations of ozone may perturb the stomata and impair stomatal functioning, resulting in increased stomatal uptake of ozone (see for example Mills et al, 2009, Global Change Biology and Wilkinson and Davies, 2010, Plant, Cell and Environment).

Reply: We refer to high ozone episodes as was modeled by Sitch et al. (Nature 2007)

Comment: 3. How long are the plants left to adapt for at each temperature level? The acclimation time between experiments should be stated.

Reply: This information was added to the text (p. 6 line 3ff). "The emission strength and the emission patterns of the VOC were modified by varying the temperature in the plant chamber between 20°C and 35°C. The temperature was changed in the morning

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before the experiment, so the plant had 7-8 h time to adjust to the new temperature under visible light."

Comment: 4. What were the growth conditions for the Holm Oak? Were these similar to the conditions the specimen was kept in during the experiment?

Reply: The conditions during growth and measurements are included in the text now (p. 5, line 28ff)

“The plants were kept in a growth room before they were used in the experiments (PPFD $\approx$ 350 – $\approx$ 500 μmol m-2 s-1, T $\approx$ 25 °C during daytime (12 h) and 0 μmol m-2 s-1 T $\approx$ 22 °C during nighttime (12 h) . They were given two days to adapt to the conditions in the plant chambers. Note that Quercus ilex and Mediterranean mixed stand were housed in two separate chambers. The chamber containing Quercus ilex was operated at PPFD $\approx$ 800 μmol m-2 s-1, the chamber containing the stand was operated at PPFD $\approx$ 480 μmol m-2 s-1. Thus the setup could be switched within one day without perturbing the plants.”

Comment: 5. What concentration of ozone is added to the aerosol chamber? This doesn’t appear to be mentioned in the methods section.

Reply: The conditions in the reaction chamber are included in the text now (p. 7, line 3ff): “During the Ox.-induced experiments Ozone levels were about 90 ppb without UV light, and they dropped to about 50-60 ppb when the UV light was turned on. In the VOC-induced experiments ozone concentrations were about 80 ppb with the UV light on and they dropped by up to 35 ppb when the plants started to emit.”

Comment: 6. Methods section, line 19 typo “details” should be “detail” Reply: Thanks, corrected.

Comment: 7. Summary section, line 26, page 4769 typo “2 degrees” should be “2 degree” Reply: Thanks, corrected

Comment: 8. Summary section, line 12, page 4770 typo “independent on emission

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patterns" should be "independent of emission patterns" Reply: became obsolete with rephrase of the paragraph

Comment: I think this is a neat and very interesting piece of work let down by weakly supported conclusions and a lack of experimental repetition. I would recommend publication with major revisions including additional experimental work. A minimum of three repetitions of each method at each temperature must be carried out in order to have confidence in the results. In addition, I would recommend that a boreal tree species is studied with the same experimental and environmental conditions and the same minimum number of repetitions to support the conclusion that SOA formation from Mediterranean species is more temperature dependent than boreal species.

Reply: The main concerns of the Reviewer consider our statements regarding the BVOC emissions, their behavior with respect to changes of PPFD and temperature as well as the variability of this biological system. Our results with this respect were indeed not written in detail and we therefore added a supplement that details such information and variations. We hope that the additional information abolish the referees concerns. We furthermore stated that the temperature dependence of monoterpene emissions from the investigated Mediterranean species is higher than that of the emissions from Boreal species. On the one hand, the finding is based on the data now given in the supplement. On the other hand, this finding is not new and was explicitly described by Staudt and Bertin (1998). We think that the information in the supplements as well as the explicit citation of Staudt and Bertin (1998) is convincing now. For a given condition in the atmosphere and as long as the BVOC mix emitted from the plants consists mainly of monoterpenes, the mass of the BVOC oxidized during the particle formation event is the dominant factor determining the mass of the formed particles. This follows from our observations described in the present manuscript as well as from the observations described in e.g. Mentel et al. (2009) and Tunved et al. (2008). Therefore the mass of oxidized BVOC is the reference for the particle mass. The mass is the reference independent of the procedure how this mass was obtained in the air

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and from this point of view the question of the repetitions for biological systems does not apply for our experiments. Leaf temperature is only an indirect variable determining particle formation, the direct variable is the concentration of the BVOC or - if transferred to atmospheric conditions - the input of BVOC from the plants to the atmosphere. The different temperature dependencies of monoterpene emissions from the Mediterranean species studied here and the Boreal species studied in Mentel et al. (2009) can directly be transferred to differences in BVOC inputs into the atmosphere. Thus, at otherwise unchanged behavior of the plants a purely temperature driven increase of monoterpene emissions is higher for Holm oak, Palestine oak and Aleppo pine than for Scots pine and Norwegian spruce. At otherwise unchanged conditions in the atmosphere the increase of particle formation from the increase of these BVOC emissions should be higher in areas covered with the Mediterranean species considered here than in areas where Scots pine or Norway spruce dominate.

As stated above we toned down our statement. We now restrict it to otherwise unchanged conditions and to the species investigated with this respect. We hope that our point is better understandable now and can be accepted together with the supplementary information.

To consider the concerns regarding missing data for Boreal species we use data from experiments published in Mentel et al. (2009). Also during these measurements the BVOC introduction into reaction chamber was modified by changes of temperature. Hence the transformation from mass dependence of particle formation to the leaf temperature dependence of particle formation just needs the temperature dependence of the BVOC emissions. This temperature dependence was measured, the number is introduced now and it is consistent with our statement.

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