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Atmospheric
Chemistry
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Discussions

Interactive comment on “CCN activity and volatility of β-caryophyllene secondary organic aerosol” *by* M. Frosch et al.

M. Frosch et al.

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Author response: We would like to thank the referees for their comments to our manuscript. We have revised the manuscript accordingly, and below we have responded to all comments. Furthermore, we have increased the symbols and errorbars in some of our figures, making them more readable (as mentioned below). These figures have been attached.

Referee 1

In the reviewed work, the authors present CCN activity and volatility results form the formation of beta-caryophyllene SOA experiments. The experimental procedure is similar to previously published works with the exception of the addition of HONO as a photochemical OH source. The results agree with previous studies and confirm that the role of OH in betacaryophyllene SOA experiments plays a significant role in the aerosol formed and its subsequent water uptake. The paper is written well and is appropriate for this journal. The figures are often too small and difficult to read. In some areas of the text, the justification of observations is vague and the arguments presented for the SOA behavior are not convincing to the reviewer. Overall, this paper does a nice job contributing supporting evidence of the CCN properties of betacaryophyllene SOA. However there are flaws in the interpretations and statements of observation. The reviewer has the following major and minor concerns.

MAJOR CONCERNS. Like the work of Asa-Awuku et al, 2009 aerosol does not activate for several hours after nucleation. Critical dry diameters are presented in fig 3 but to what fraction do the larger particles (>100nm) grow? In this region, a critical diameter may not be obtained but particles can grow. The change in activated fraction may also be indicative of droplet growth that may be inhibited. Asa-Awuku et al, show that it takes considerable time for droplets of a given dry diameter to activate into droplets similar to that of ammonium sulfate at 100nm. Is this also true of the aerosol formed in this system? If so, the consideration that no kinetic inhibition exists may need to be revised. If kinetic inhibition does exist such that droplets less than 0.75 microns (the lower detection limit of the CF-CCNC OPC) are formed at the exit of the column, they will not be counted. This will bias all CCN/CN fractions and TDGA. The authors should reconsider their statement that no kinetic limitations exist.

Author response: As explained in page 20755, line 10, we were careful to have SOA number concentrations sufficiently low to avoid depletion of water vapor in the CF-CCNC, which could affect the size of growing or activating droplets. However, it is possible that particles larger than those selected for CCN experiments might take up water and grow, and that their behaviour might be different from that of ammonium sulphate. We have therefore included these considerations on page 20763, line 24, which now reads: "However, the lower size limit for detection in the OPC of the CF-CCNC is

750 nm. If kinetic inhibition exist to an extent that growing droplets do not reach this size, different instrumentation would be needed to detect their water uptake." Most of our data are obtained after several hours in the smog chamber and we have therefore softened the statement on kinetic limitations: In the abstract (page 20746) we have modified the last sentence, as follows: “Using the method of Threshold Droplet Growth Analysis it was also concluded that the activation kinetics of the SOA do not differ significantly from calibration ammonium sulphate aerosol for particles aged for several hours." On page 20764, lines 8-19 we have changed the text to: "Asa-Awuku et al. (2009) observed an initial delay in activation kinetics, so that more than 6 hours of chemical ageing were required for the growth kinetics of SOA particles to be comparable to those of ammonium sulphate. We do not see indications of delayed droplet growth kinetics, but it should be noted that we only have very few data during the first five hours after VOC injection and that these data are for much higher supersaturations (1.51% and 1.41% respectively) than those discussed by Asa-Awuku et al. (1.02% and 0.61% respectively). Furthermore, if kinetic inhibition exist to an extent that growing droplets do not reach the lower size limit for detection in the OPC of the CF-CCNC of 750 nm, different instrumentation are needed to detect their water uptake." On page 2765, lines 13-16 we have inserted the following: "Investigation of CCN activation kinetics revealed that growth and activation of aged SOA particles were comparable to those of ammonium sulphate particles and therefore not kinetically hindered ."

Page 20753, line 27. I would also be hesitant to assume that the chemical composition of the gas phase in the SD-CCNC is similar to the gas phase of the flow coming directly from the smog chamber. Humidity conditions, condensation and adsorption of gas molecules on particles and the CCNC SS influences on gas-particle re-partitioning are not characterized.

Author response: The CF-CCNC was operated both with and without the dilution system without it having any discernable effect, but we agree that the conditions mentioned by the referee could affect measurements. We have therefore changed the text to the following: “To obtain a sample to sheath flow ratio of 1:10, dilution of the sample flow after the DMA was necessary. This was done by sending the exhaust from the SD-CCNC (3 l/min) through a diffusion drier and a particle filter and adding it to the flow of 0.8 l/min exiting the DMA. This dilution system was used during the fraction of each experiment when the SD-CCNC was running (up to eight hours in experiments lasting up to 30 hours). Turning off the SD-CCNC and disconnecting the dilution system did not change the fraction of activated particles, i.e. the ratio between the number concentration of activated particles (measured with the CF-CCNC) and the total number concentration (measured with the CPC). It was therefore assumed that the chemical composition of the gas phase in the exhaust of the SD-CCNC was similar enough to the gas phase of the flow coming directly from the smog chamber, that dilution did not alter partitioning between particle and the gas phase in the aerosol flow.”

Page 20758, line 28. This section of the text is somewhat confusing. For one, the authors do not give a speciïňĄc residence time of the SD-CCNC, and the residence time in the TD (6.2 s) is similar to that in the CF-CCNC (8 s).

Author response: One reason for using the TD was to investigate if exposure to elevated temperatures could explain the discrepancy between the CF-CCNC and the SD-CCNC. The purpose of the TD is therefore to mimic the conditions in the CF-CCNC, and comparison of residence times is therefore highly relevant, mainly for the TD and CF-CCNC (since the SD-CCNC operates below room temperature). However, to avoid confusion, the last two sentences in the paragraph have been omitted.

Page 20760, line 24-28. The stated comparison between the results of Alfarra et al (2012) and Tang et al. (2012) should not be made since the precursor concentrations are vastly different. Considering that Tang et al. also observed that there were no obvious variations of hygroscopicity when precursor concentration was above 50 ppb, the two results are actually consistent with each other.

Author response: We agree with the reviewer and the comparison between Alfarra et

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al. and Tang et al. has been removed. The text now reads: "Alfarra et al. (2012) carried out photo-oxidation at two different initial β-caryophyllene concentrations, 50 and 250 ppb, but did not observe any influence of precursor concentration on hygroscopicity, which is in contrast with the findings for SOA generated from photo-oxidation of α-pinene by Duplissy et al. (2008)."

Why does the hygroscopicity of aerosol measured with the SD-CCN decrease in Fig 4a? Little discussion is provided on this interesting phenomenon.

Author response: Results or particles from experiments with the addition of an OH scavenger (experiments a and b) are shown in Fig. 4a: No systematic relation between CCN activity and volatility beyond experimental uncertainty (as represented by the error bars in Fig. 4a), was detected. There seem to be a decrease in CCN activity with time, but given the magnitude of the errorbars no firm conclusions can be made on this bases and we suggest this is addressed in future studies.

Page 20758, line 27: After the TD, are the particle and stream temperatures at the inlet of the SD-CCNC the same as those without passing a TD? The authors need to make sure that the particle and stream temperatures under different experimental conditions are the same at the CCNC inlet to make comparisons.

Author response: Temperature was measured at the inlet of the CF-CCNC (not at the SD-CCNC inlet), but since the lengths of tubing between the TD and the two CCNCs were of equal magnitude, the temperature at the CF-CCNC inlet is representative of the temperature at the SD-CCNC inlet as well. We could not identify any TD influence on the inlet temperature We have therefore added the following text to page 20755, line 26: “Equal aerosol sample temperatures at the inlet of the CCNC instruments were crucial for a valid comparison of the measurements with and without TD. The tubes between the TD and the two CCNC’s were of equal length and we assume the two inlet temperatures to be the same. The temperature of the aerosol flow was measured at the inlet of the CF-CCNC and was found to be independent on TD temperature and flow type (i.e. TD inline or bypassed). This indicates that the temperature of the aerosol flow entering the SD-CCNC and CF-CCNC after passing through the TD had same temperature as an aerosol flow bypassing the TD."

In addition, the reviewer is not entirely convinced that Fig 5 provides sufficient evidence of the following, "L9. Observations indicate that SOA generated under light exposure is not volatile or that compounds contributing to CCN are not highly volatile". How does the volatility profile of the SOA change with time?

Author response: Our claim regarding light exposure and volatility is based on Fig. 6, not Fig. 5. By comparing Figs. 6 and 4b it is seen that the connection between CCN activity and TD temperature is definitely not as clear for particles exposed to light, as it was for particles not exposed to light (in Fig. 4b). Also, data from Fig. 4 do not indicate any temporal variation in SOA volatility. However, we do agree that our dataset does not allow us to evaluate the temporal variation of volatility for SOA exposed to light. We have therefore modified the statement as follows (page 20761, line 12): "Precluding effects of temporal variations in volatility, these observations indicate that SOA generated under light exposure is less volatile than SOA generated without light exposure, or at least that the compounds contributing to the CCN activity are not highly volatile in particles generated under exposure to light."

In Fig 5b. The aerosol becomes significantly more hygroscopic with time; especially during the first 10 hours shown in Fig 6. Since, TD and Bypass data are not preformed simultaneously it is difficult to the compare the temporal trends. Is it not also plausible that the thermal denuded aerosol of a more hygroscopic particle at 2.5 hours can be more hygroscopic than the particle a bypassed particle at 2 hours (sometime before)? The last few points after 7 hours (once composition stabilizes?) in the CF-CCNC may suggest that the aerosol hygroscopicity is susceptible to temperatures when formed with light. The reviewer would appreciate clarification.

Author response: We agree that there is a relation between CCN activity measured with the CF-CCNC and SS (i.e. temperature) in the instrument for all experiments (including those with lights on). This is discussed in Section 4.3. Simultaneous determination of heated and unheated aerosol would have been desirable, but not necessary. However, Fig. 6 shows 2-3 points for each of the “TD modes” which enables us to evaluate trends and interpolate for the first ∼10 hours. Based on this we therefore conclude that, within the accuracy of our measurements, a thermal denuded aerosol of a more CCN active particle is not more CCN active than a “non-denuded” particle measured half an hour earlier.

Lastly, how much does temperature in the chamber change from the addition to lights? This could also effect the SOA formation processes. Perhaps the authors could also show this in Fig. 6.

Author response: The lamps producing UV light influenced only temperature in the smog chamber, not in the adjacent lab where the instruments were placed. However, the lamps did cause a slight increase in temperature of about 5 °C (from 20 to 25 °C, as also mentioned in Sect. 3.1). Since the lamps were turned on almost simultaneously with VOC injection and were on during the entire measurement, temperature was constant during all experiments. Text emphasizing this has been inserted on page 20752, line 26: "Temperature was constant for the entire duration of each experiment; the effect of this slight temperature increase on the formation and properties of SOA generated under exposure to light was considered negligible."

OTHER CONCERNS: Page 20759, line 22. What experimental uncertainties? Author response: For clarification, the following text has been inserted on page 20758, line 22: “as represented by the error bars in Fig. 4a,”

Page 20759, line 19. Tang et al, 2012 were able to show that reaction s with OH produced aerosol of higher hygroscopicity and increased oxygenated content (O/C) Author response: For comparison, we have added the following: “This may be linked to the finding by Tang et al. (2012) who related the presence of OH during oxidation to the formation of particles of higher oxidation state and increased hygroscopicity."

Fig. 4. The symbols are too small and it is difficult to see the difference between open and closed symbols. In 4b, it is difficult to distinguish the squares from the circles.

Author response: We have increased the size of the symbols and errorbars in Figure 4a and 4b, as well as in Figs. 5a, 5c, 7, 9 and 10a-d.

Page 20762, line 13. How significantly with dilution?

Author response: We have added the following text: "For example, the concentration dependency of water activity for a number of atmospherically relevant organic-inorganic mixtures at concentration ranges relevant at CCN activation are listed in Frosch et al., 2011."

Page 20762, line 27. Heterogeneous chemical reactions may also play a role in chemical aging under dark ozonolysis conditions Fig. 8. What is the significance of a fit to the -1.2987 dependence? What will a forced fit with exponent -1.5 look like?

Author response: For comparison, we have added a forced fit with exponent -1.5 to the figure.

Referee 2

The paper discusses the trend in hygroscopicity of b-caryophyllene SOA under supersaturated conditions using k_CCN as a primary diagnostic of CCN activity. It appears to be largely motivated by the Asa-Awuku et al. (2009) study and borrows strongly from the methodology therein. The key differences appear to be the range of experimental conditions (e.g. presence / absence of OH scavenger, addition of illumination or an additional OH source in HONO). There is broad agreement with previously published work, but some discrepancies. Whilst the study is predominantly observationally driven and remains largely inconclusive, the experiments seem to have been carefully conducted and are worthy additions to the literature. I recommend publication of the manuscript once the authors have considered and responded to the following comments (in addition to those of the first referee):

On page 20758, the last paragraph seems to ask more questions than it answers and indicates apparent inconsistency between the TD measurements and the hypothesis of Asa-Awuku that was used to explain the SD-CCNc and CF-CCNc discrepancy in terms of volatility. The last full paragraph on p20762 seems to provide further evidence to counter the argument that volatility alone can explain the discrepancy. Whilst it is clearly important simply to report the observations, it would be useful for the authors to indicate the most likely of the alternative explanations suggested and possible experimental / interpretational strategies to investigate them.

Author response: We believe that understanding SOA volatility is key to understand the observed discrepancies, and have inserted this on page 20758: "The reason for this may be related to effects of the relatively high temperature in the CF-CCNC, which is discussed further in Sect. 4.3." Furthermore, we have expanded the perspectives on page 20765 to include more possible strategies for answering the many unknowns: "In future studies, determining the volatility of β-caryophyllene SOA could provide a better understanding of this dependency. Yet, other explanations could involve a size dependency of the particle composition."

In the paragraph starting on line 7 of page 20758, the authors stop short of stating that the Tang et al measurements were in error, but the tone clearly implies mistrust of them. Do they have any means of rationalising the discrepancy between their study and the Tang measurements?

Author response: The main difference between the study by Tang et al. and ours (as well as the quoted studies by Asa-Awuku et al. and Alfarra et al.) is the much larger smog chamber as well as the lower precursor concentration and a slightly higher temperature. We did not intent to imply mistrust in the experiments of Tang et al. We have therefore rephrased the paragraph to modify the tone: "Tang et al. (2012) examined

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SOA from low initial concentrations of β-caryophyllene (5-20 ppb) in a larger chamber (xx m3) and did not detect any temporal trends in the CCN activity of SOA generated in the absence of an OH scavenger. They consistently observed high κCCN values (0.13-0.25), ascribed to the low precursor concentrations resulting in SOA mainly composed of highly oxidized compounds of high hygroscopicity and CCN activity. This is consistent with the conclusions of Duplissy et al. (2008). The differences between results of Tang et al. and this study (and Asa-Awuku et al.) are surprising and interesting and should be investigated further."

p20754, lines 9-11, can the authors expand on the avoidance of problems associated with multiple charging? Since determination of Ddry;c requires a fit to activated fraction at all diameters, surely all diameters with activated fractions > 0 need to be above the modal diameter to avoid multiple charges being a problem at some point in the fit. Does this not place a very low limit on maximum supersaturations that can be used and still avoid multiple charge problems? The modal size does not appear to be small enough to avoid this problem. Or do these lines only apply to the "fixed Ddry" method and only for the SD-CCNc as described in line 20 p 20753? If this is the case, the authors need to explain clearly how they ensure that multi-charge correction is carried out accurately when using the "fixed S" method with varying D, particularly for the CF-CCNc (e.g. how are the diameters matched between doubly and triply charged particles and their corresponding singly charged bins - is it an interpolation between bins or an exact match of diameters at high resolution?). There can be very great sensitivity of critical supersaturation and Ddry;c to the accuracy of the correction depending on the distribution shape.

Can the authors comment on whether the magnitude in the difference of supersaturation dependent k shown in Figure 4b from the "fixed S" method using the monodisperse CF-CCNc can be influenced by incorrect multiple-charge correction because of the difference in how close to the modal diameter the Ddry;c is found? Is propagation of the maximum error from multi-charge correction able to explain the discrepancy in predicted CCN activity between "fixed Ddry" SD-CCNc and "fixed S" CF-CCNc analyses?

Author response: We will address the two comments above collectively: Multiple charging was considered both in the case of fixed D_dry and fixed SS_c, and was accounted for using the approach of Prisle et al., 2008. This approach was used for all measurements, both from the SD-CCNC and the SF-CCNC (this has now been emphasized on page 20754, line 11). "For all reported experiments, Ddry,c as well as SSc were determined by correcting for doubly charged particles and fitting the activated fraction as a function of dry particle diameter or supersaturation, respectively, to a sigmoidal function, similar to the approach of e.g. Prisle et al. (2008)." Choosing diameters close to or above the modal diameter did, of course, limit the choice of possible supersaturation somewhat – especially at the end of experiments, when particles had grown to considerable sizes. However, at the end of the experiments (up to 30-40 hours after initial VOC injection), absolute particle concentrations had decreased due to wall losses. To avoid uncertainties associated with such low concentrations, it was therefore anyway necessary to choose sizes close to the modal size. We therefore chose to focus on a limited number of diameters to optimize data quality. For the same reasons, for the fixed SS_c experiments, we mainly focused on values of SS high enough to measure at diameters above the modal size.

Though it is noted in the text, the authors offer no suggestion as to why the Ddry;c of particles at supersaturation 1.51% lies above those at 1.02 and 0.6% made using the CF-CCNc in ozonolysis experiments with no butanol reported in Figure 3. Can they speculate as to a cause? Is it some obvious error, or expected variability? The figure resolution should be improved to enable them to be read at reasonable magnification.

Author response: We do not believe it to be an error, since the data have been carefully checked, and the variation is also well beyond any expected variability. Although the cause in not fully understood and should be in focus of further investigations, we hypothesize that the high temperature at SS 1.51% in the CF-CCNC is responsible for the decrease in kappa. To emphasize this, we have inserted the following text at page 20758, line 6: “The reason for this may be related to effects of the relatively high temperature in the CF-CCNC, which are discussed further in Sect. 4.3” Futhermore, the discussion in Sect. 4.3 has been expanded: "This effect of temperature on particle composition as well as on size is a likely explanation of the puzzling behaviour observed in Fig. 3a: That at SS = 1.51%, particles had a higher Ddry,c than at SS = 0.60% and 1.02%. However, if volatility was the only factor governing the change in κCCN, measurements performed with the SD-CCNC should consistently result in higher κCCN than measurements performed with the CF-CCNC. This is the case only for particles generated in experiments a-e (without exposure to light). Therefore, a thorough study of volatility of SOA from β-caryophyllene oxidation would be helpful in understanding the observed values of κCCN."

Minor comments: p20747 line 25: The ïňĄrst and second parts of the sentence are not linked appropriately such that it is a non-sequitur; it should be rewritten. Also, Hamilton et al., 2011 and Jenkin et al., 2012 should be cited in the ïňĄrst part of the sentence.

Author response: The sentence have been changed as follows: Products from oxidation of β-caryophyllene have been the focus of previous studies (e.g. Jaoui et al., 2003; Lee et al., 2006; Chan et al., 2011; Hamilton et al., 2011; Jenkin et al., 2012). It has been shown that both the aerosol yield and physical properties, such as hygroscopicity and CCN activity, of SOA depend strongly on experimental conditions (Donahue et al., 2005; Huff-Hartz et al., 2005; Asa-Awuku et al., 2009; Alfarra et al., 2012; Tang et al., 2012).

p20748, line 19 - in this sentence, the main point leading to b-caryophyllene SOA having a higher Mw and lower O:C is that the earlier generations of oxidation product are lower volatility than monoterpene parent VOCs, so the products can condense with a lower degree of oxygenation. This should be mentioned prior to this sentence. It would have been useful for the kGF to have been reported from measurements of subsaturated water uptake using one of the HTDMAs available at PSI for comparison

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with the Alfarra study. Were there no HTDMA measurements?

Author response: Unfortunately, for the experiments no HTDMA was available. The discussion of the consequences of the extra isoprene unit on the molar mass and O/C (previously found in p29748, line 20) has been moved to p20747, line 24: "Products from oxidation of β-caryophyllene have been the focus of previous studies (e.g. Jaoui et al., 2003; Lee et al., 2006; Chan et al., 2011; Hamilton et al., 2011; Jenkin et al., 2012). Since sesquiterpenes contain one more isoprene unit than monoterpenes, oxidation products of sesquiterpenes generally have a higher number of carbon atoms and a higher molar mass. It has also been shown that both the aerosol yield and physical properties, such as hygroscopicity and CCN activity, of SOA depend strongly on experimental conditions (Donahue et al., 2005; Huff-Hartz et al., 2005; Asa-Awuku et al., 2009; Alfarra et al., 2012; Tang et al., 2012)."

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C12414/2013/acpd-12-C12414-2013-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 20745, 2012.

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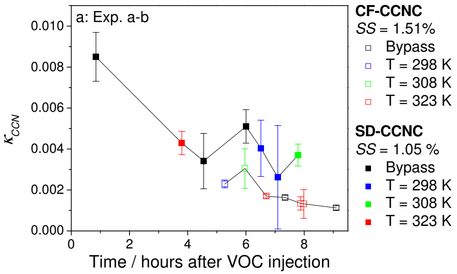

Fig. 1. Fig. 4a revised

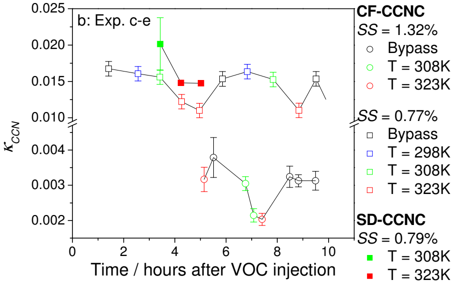

Fig. 2. Fig. 4b revised

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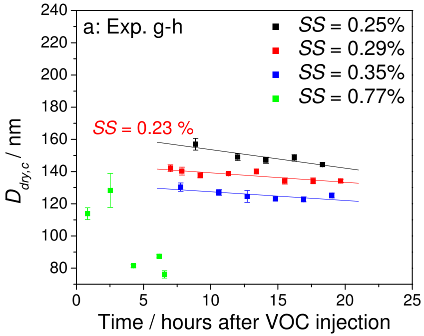

Fig. 3. Fig. 5a revised

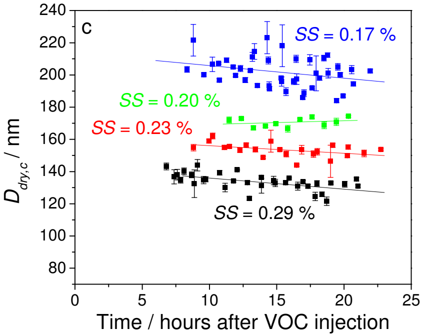

Fig. 4. Fig. 5c revised

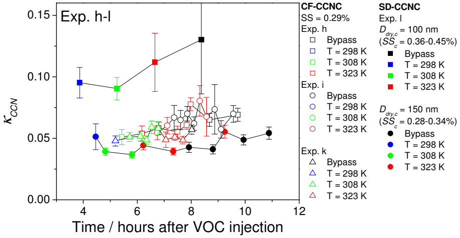

Fig. 5. Fig. 7 revised

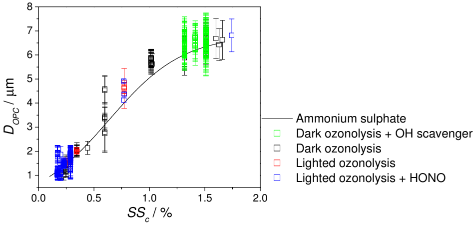

Fig. 6. Fig. 9 revised

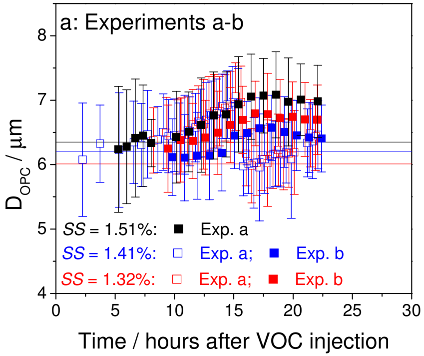

Fig. 7. Fig. 10a revised

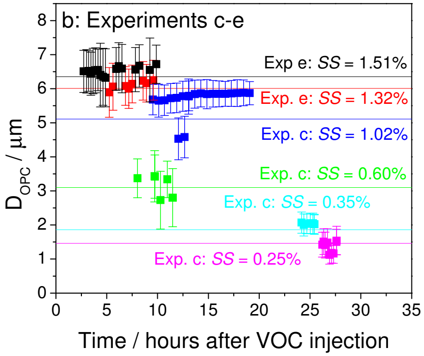

Fig. 8. Fig. 10b revised

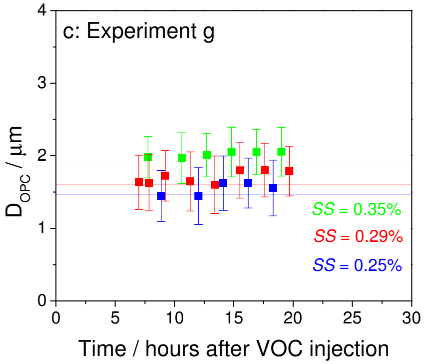

Fig. 9. Fig. 10c revised

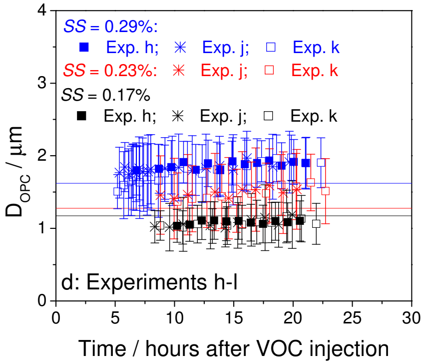

Fig. 10. Fig. 10d revised