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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Suppression of new particle formation from monoterpene oxidation by NO_x” *by* J. Wildt et al.

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We thank both referees for their helpful comments. All their suggestions were considered and we believe that the changes made according to the comments of both referees substantially improved the manuscript. In the following we give our responses to each of the referees’ comments.

Referee #. 1: Comment 1: CPC cut-off diameter of 7 nm: The particle formation rate is always given as J_7 and it is stated that the CPC (TSI 3025A) starts detecting particles at a diameter of 7 nm (p.25834 l.15-17). TSI gives the lower detection diameter for the 3025A UCPC as 2.5 nm or 3.0 nm and in Mentel et al., 2009, a lower size of 3.0 nm is

stated. Why do you assume 7 nm?

Response: Referee # 1 is correct; the TSI 3025A CPC detects 3 nm particles. However, the UCPC 3025A used for the measurements presented in Mentel et al. 2009 was meanwhile exchanged by a TSI 3022A with a 7 nm cut off. The information on the particle diameter of 7 nm was correct, the information on the type of CPC used was wrong. We thank referee # 1 for finding this error. “3025” (page 25834, line 15) is now exchanged by 3022. Furthermore “UCPC” is exchanged by CPC.

Comment 2: Wall losses influence nucleation rate, growth rate, SOA yield, PM_MAX: This comment is especially important in case the 7 nm cut-off diameter is correct, but needs to be considered also if the cut-off diameter is 2.5 or 3.0 nm. In all situations where the growth rates for the particles are low, the first detection of particles is decoupled from the original nucleation and there are many minutes or even hours between the nucleation and the detection. This time lag varies strongly with the particle growth rate and it influences the observed particle concentration, the derived nucleation rate, the SOA yield and PM_MAX because the wall losses of the condensing vapours as well as the size-dependent wall losses of the particles in the range between molecular size and 7 nm (as well as removal of particles by flow out of the chamber) depend on this time lag (see Kerminen and Kulmala, J Aerosol Sci., 2002; Ehrhart and Curtius, ACP, 2013). For long lag times J7, SOA yield and PM_MAX are underestimated compared to a situation without wall losses and quantitative statements such as the slope of -2 in Fig. 10 as well as the exponent of 2.3 (p25839, l.27) become dependent on the size of the reactor chamber and other factors like the rotation speed of the mixing fan. In a stirred reactor of ~1.5 cubic meter the wall loss life time of condensable gases will be on the order of one minute and therefore the nucleation and growth of the particles is in strong competition especially for those cases where the NPF is observed 2-5 hours after the start of the OH formation. Have these loss rates been determined? How are they included in the determination of J, etc.? If the derived slope in Fig 10 is not -2, then also the statements about the mechanism and the role of first generation peroxy radicals as well as higher generation peroxy radical like molecules have to be reconsidered (e.g. Sect. 5.1.4).

Response: We fully agree, wall losses impact measured nucleation rates, growth rates, particle mass formation from BVOC oxidation and time lags. In particular J7 was substantially affected by wall losses. However, this was impossible to be measured with the equipment available during our measurements. Only with the help of recently developed instrumentation (Particle Size Magnifiers) such wall losses are measurable now. As we have now quantified these losses by using this new instrumentation, the strong impact of wall losses on J7 in our chamber is now known and considered. The method of considering wall losses as well as our method estimating error bars for J7 is described in detail in the new Section S7 of the Supplement. We did not add this information to the manuscript because we feel that the bulk of explanations will destroy the text flow and might diverse the reader from the central point of the manuscript to a side track.

The text in the Supplement reads:

"Determining rates of new particle formation (J7) from chamber data requires consideration of wall losses and of background particles. Both may skew determinations of J7 if their impact on J7 is substantial. We used BVOC concentrations around 10 ppb and, as also found in other studies (e.g. Mentel et al., 2009, Mentel et al., 2013), formation of new particles from ozonolysis alone was low as long as BVOC concentrations in that range were applied. Therefore also the background particle number concentration formed from ozonolysis of alpha-pinene and from the OH formed during ozonolysis was low. Without NOx addition the particle number concentration (PN) of the background ranged between 100 cm-3 and 300 cm-3. Background PN was quite constant during individual experiments with fluctuations < 10 %. Inducing NPF by OH formation (TUV lamp on) increased PN to ∼3×104 cm-3 (see Fig. 3 in the manuscript, red trace). Since the maximum PN was much higher than fluctuations of background number concentrations, J7 was not substantially skewed by background particles, since it

was determined from the slope of PN versus time. NOx addition to the chemical system decreased J7 as well as the background particle numbers. At [NOX] $\geq$ 40 ppb, background PN were between 3 cm-3 and 7 cm-3 and fluctuated from ∼1 cm-3 to ∼11 cm-3. Compared to the maximum PN determined during NPF events at [NOx] $\geq$ 40 ppb (130 - 2200 cm-3) these fluctuations are still small. Assuming that no particles were introduced into the chamber and all background particles were produced in the chamber we estimate the upper limit of 7 nm particles formed as background using the maximum particle number of 11 cm-3 and the residence time of the air in the chamber (63 min). This results in max. background J7 ∼0.0032 cm-3 s-1. This is by far lower than the lowest J7 determined during our experiments. Considering this as worst case estimation, we assess possible errors in J7 determinations due to background particles as low over the whole range of applied NOx.

To estimate the impacts of wall losses on J7, the following experiment was conducted using two different CPCs in parallel. One was a TSI 3022A with a cut off diameter of 7 nm, the other one was a TSI 3786 coupled to a particle size magnifier (PSM, Airmodus A09) with a nominal cut-off diameter of 1.5 nm for the PSM/CPC system. Ten ppb alpha-pinene and 80 ppb O3 were added to the chamber (without NOX addition). Before starting the photolytic production of OH radicals, the system was in steady state showing stable number concentrations around 130 cm-3 particles > 1.5 nm and ∼11 cm-3 for particles with diameters > 7 nm. Short after photolytic production of OH radicals, PN measured by the PSM increased rapidly to ∼1500 cm-3 within about 1.5 minutes. Then the OH production was switched off and PN as measured with the PSM decreased exponentially indicating a first order loss process (loss coefficient - 0.0017 ± 0.0001 s-1, R2 = 0.9, τ = 9.8 min.). PN as measured with the 7 nm CPC stayed constant at ∼11 over the whole measurement period proving that particles with diameters > 7 nm did not substantially contribute to PN during that experiment. From this we conclude that the exponential decay observed for the number concentration of particles with diameters between 1.5 and 7 nm was mainly due to wall losses of small particles. The loss coefficient of 0.0017 s-1, equivalent to a lifetime of about 10 minutes, indicated that wall losses in our chamber had substantial impact on the observation of formation rates of new particles. To consider the impacts of wall losses, J7 was determined in the following manner. It was assumed that new particle formation and wall losses were the dominant processes and that impacts of outflow and coagulation on PN were negligible. This led to the approach:

J7=∂(PN)/∂t + L(PN) (ES29)

In equation ES29, ∂(PN)/∂t is the first derivative of the measured PN as a function of time at the inflection point. L(PN) is the loss rate and calculated as product of loss coefficient and PN at the respective inflection points. Depending on the experiment the contributions of ∂(PN)/∂t and L(PN) to J7 were different. At high∂(PN)/∂t, L(PN) and ∂(PN)/∂t were similar in magnitude indicating that even at the fastest temporal increases of PN, J7 were already affected by wall losses. At the lowest measured ∂(PN)/∂t, L(PN) exceeded ∂(PN)/∂t by a factor of 6 indicating that for small ∂(PN)/∂t the loss rates dominate ∂(PN)/∂t. Hence, the uncertainty of wall losses determines the error in J7. Therefore different wall losses were used to calculate uncertainty limits for J7. We estimated the uncertainty limits for J7 by doubling and halving the measured loss coefficient, respectively. The upper limit was estimated using a loss coefficient of 0.0034 s-1 corresponding to a lifetime of 5 minutes. The lower limit for J7 was estimated using a loss coefficient of 0.00085 s-1 corresponding to a lifetime of 20 minutes." End of text cited from the new Section 7 of the Supplement

The recalculations of J7 led to substantially increased numbers for all J7 causing a general shift to higher values. Due to higher impact of wall losses at lower J7 also the numbers for the slopes of power law dependencies had to be recalculated: The slope given for ln(J7) in dependence of ln(BNR) (page 25839, line 27) changed from 2.3±0.1 to 1.9±0.1. The slope of ln(J7) in dependence of P(O3) (Fig.10) changed from -1.9±0.37 to -1.6±0.27.

The changes in power law dependencies were not substantial and gave no reason

for reinterpretation of our main results. On the contrary, these data were very robust versus changes of wall losses. Even when exploiting the whole range of the broad error limits given now for J7, the power law dependencies remain similar. As example: Calculating the slope for ln(J7) in dependence of ln(BNR) assuming wall losses to be twice as high as the measured wall losses leads to a slope of 1.74 ± 0.1 instead of 1.9 ± 0.1. Calculating the same with the assumption of wall losses being $\frac{1}{2}$ of the measured wall losses leads to 2.0 ± 0.1 instead of 1.9 ± 0.1. The robustness of the power law dependencies versus broad variations of wall losses leaves the proposed mechanism as the most probable explanation for our findings.

Other actions with respect to the changed data for J7: All figures, tables and the text now include the numbers for J7 corrected for wall losses.

As the degree in suppression of J7 by NO is lower than estimated before, the phrase "three orders of magnitude" was exchanged by the phrase: more than two orders of magnitude.

The numbers given for J7 in Section S6 of the Supplement (Sensitivity tests) were exchanged by the corrected numbers for J7 (0.13 cm-3 s-1 instead of “0.02” cm-3 s-1 for the lowest J7 and 66 cm-3 s-1 instead of “42” cm-3 s-1 as average for the data obtained without NOX addition). This procedure changed the [RO2] necessary for allowing first generation RO2 permutation reactions to be rate limiting for J7 from “13.7” ppb to 6.8 ppb. Furthermore a sentence was added considering that J7 might be dependent on [RO2] to the power of 1.6 instead of 2. This text reads: Assuming that the dependence of J7 on [RO2] would be to power law of 1.6 instead of 2 would lead to even higher [RO2] of 49 ppb. Both values for [RO2], 6.8 and 49 ppb are unrealistic high even when....

As in either case [RO2] remains unrealistic high, the basic result given in Sect. S6 is conserved. Consistent to the consequences from the calculations shown in Section S4 and S5, our supposed mechanism holds. Permutation reactions of first generation peroxy radicals cannot be the rate limiting step in new particle formation. The only possibility to explain our findings is that permutation reactions of higher generation peroxy radical like intermediates limit J7.

As the error margins of slope of ln(J7) in dependence of P(O3) do not exactly cover -2 the phrase "power law dependence with an exponent of approximately -2" Is exchanged by the phrase: power law dependence with an exponent approaching -2.

Furthermore the text on page 25847, lines 3 – 7 was completed with this respect and now reads: The observed relationship between (J7) and P(O3) indicated a mechanistic inverse coupling between J7 and P(O3). Considering the competition of reaction pathways R2 and R3, the simplest way of explaining the coupling would be a direct involvement of PRP in NPF. Since P(O3) is a linear measure of [RO2] and P(PRP) is proportional to the square of [RO2], P(PRP) should decrease in a squared manner with respect to increases of P(O3). This would suggest power law dependence with a slope of -2 which is somewhat steeper than the measured slope. Nevertheless, losses of intermediate particle precursors apart from the pathway of new particle formation can easily explain attenuation of slopes for power law dependence. From the substantial nonlinearity indicated by the relationship between J7 and P(O3) as well as from the substantial nonlinearity of the relationship between J7 and BNR we conclude that PRP are involved in NPF.

Our response to the referees comment with respect to impacts of wall losses for other quantities:

PMMAX was obtained when the particles had diameters larger than 100 nm. For such large particles wall losses in our chamber are much smaller than for small particles and negligible compared to the flush out rate which was considered (details see Mentel at al., 2009). Therefore wall losses were neglected for our interpretations of PMMAX. Please note that we basically use relative data for our interpretation. There was no substantial impact of NOX on PMMAX as long as [BVOC]0/[NOX]0 was larger than ∼5

ppbC/ppb. This finding is independent of wall losses as long as the wall losses are constant in all experiments.

Growth rates: we give no quantitative data on growth rates. Possible errors in quantitative data of growth rates are therefore of minor importance.

Time lags: similar as for growth rates. We do not use any quantitative data on the time lags for interpretation. Impacts of wall losses on the time lags are therefore not important.

Comment 3: Which are the smallest NPF rates that can be reliably measured? Formation rates J7 of 0.02 cm-3 s-1 are listed in Table 1.

Response: We do not know this because it was not tested yet. The smallest J7 given now (0.13 + 0.9 – 0.5) indeed has large uncertainties. But, our conclusions are based exploiting the high dynamic range of J7 which varies by a factor of ∼500. Therefore even high error limits for small J7 do not carry too much weight for our main result (see above, estimates of impacts of different wall losses on slopes of double logarithmic plots).

Comment 4: How high are background particle concentrations before start of an experiment?

Response: Background particle concentrations depend on BVOC and NO concentrations. At ∼ 10 ppb BVOC and without NO, the background was between 100 cm-3 and 300 cm-3. At high NO, the background was between 3 and 7 cm-3 see also our new Sect. S7 in the Supplement.

Comment 5: How large are NPF rates (e.g. from contaminant H2SO4, as stated on p. 25853) when all lights are switched on and only ozone and water vapour are added but no BVOCs? How reproducible are measurements of background NPF?

Response: At zero concentrations of organics in our chamber J7 is below any measurable value. For comparison see also Mentel et al. (2009) where threshold concentrations are shown for BVOC below which no new particle formation is observable.

Comment 6: Please add error estimates and error bars for all data of Figures 4-10.

Response: Error limits were added whenever sensible. The necessary information on the estimated error bars is added to the figure captions. Our responses are given explicitly for each figure and the text added to the figure legends:

Figure 4: Error bars added for [NOX], [O3], and [OH]. The figure caption now reads: Fig. 4: Temporal behavior of [NOx] (brown circles, left scale, ± 8%), [O3] (blue squares, left scale, ± 2 ppb), particle number concentration (green line, right scale, multiplied by 104 for clarity), and [OH] (black bars, right scale, ± 20%) in an experiment with [NOx]0 ∼40 ppb . . .. . .

Figure 5: Error bars added for P(O3) and for J7. Added text in the figure caption reads: . . .. Errors in P(O3) were estimated to be ± 2.5 ppb h-1. Errors in J7 due to wall losses and background particle numbers were estimated as described in Sect. S7 in the Supplement.

Figure 6: Error bars added for [OH]. Furthermore, according to comment no. 15 of referee #2 a color code was used to differentiate between classes of [BVOC]0. The figure caption now reads: Fig. 6: OH concentrations measured during the first hour after switching on the TUV lamp in dependence of [NOx]0 (note logarithmic scale of x-axis). The error in OH concentrations is estimated to be ± 20 %. Brown circles represent OH measured at [BVOC]0 < 55 µg m-3, blue circles those measured at 55 < [BVOC]0 < 65 µg m-3 and black circles those measured at [BVOC]0 > 65 µg m-3. The red square shows the OH concentration measured for the experiment with the highest NOx ([NOx]0 =103.5 ppb), 5 hours after ignition of the TUV lamp. After that time, new particle formation was observed, [O3] had increased to 85 ppb and [NOx] had decreased to 26 ppb.

Figure 7: Error bars added for PMMAX,norm and for P(O3). Added text in the figure caption reads: . . . The error in PMMAX,norm is mainly due to the extra- and interpolations to [BVOC]0 = 65 µg m-3 and estimated to ± 12%.

Figure 8: Error bars added except for the reference points. Added text in the figure caption reads: As J7 for [NOx] ∼ 0.3 (reference points) was forced to be 1, no error limits are given for both reference points. Other errors are determined from error propagation setting the error for the reference points to zero.

Figure 9: No error bars added to keep the clarity of the figure. Added text in the figure caption reads: Errors in [NOx] (± 8 %), [O3] (± 2 ppb), and [OH] (± 20 %), are estimated as before but not shown for clarity. Errors in absolute values of [RO2] are not shown because they are unknown. These errors depend on the error of the average rate constant for the mix which is unknown.

Figure 10: Error bars were added but only for the data points used for the fit. Added text in the figure caption reads: Error bars added only to data points used for the fit. Note that for P(O3) approaching the significance level, the error of the logarithm approaches -∞.

Minor comments:

p.25836 l.5: What is the detection limit of the NOx monitor?

Response: The required information is added in Section Experimental, former page 25833. The text reads: Two different systems were used. During a first period of the measurements a system with a detection limit of ∼200 ppt at integration times of 100 s was used. During the later phases we were able to use a system with an improved detection limit of ∼10 ppt at 30 s integration time.

Technical corrections: Supplement:

p.5, l.13: change to ": : :is an increasing: : :" Thanks, done.

p.12, l.26: change to ": : :had no substantial impact on results: : :" Thanks, done.

p.13, l.5 “range” Thanks, done.

Referee No. 2:

Comment 1: The measured particles are down to 7 nm, which is well above the size of newly nucleated particles. So it is not clear that the permutation reactions are responsible for particle formation or growth or both. This needs to be stressed and perhaps reflected in the paper title as well.

Response: In principle this comment is correct. However for our argumentation it is not important if NOx indeed supresses the nucleation rates or the growth to 7nm (which is what we believe), the effect is similar: particles cannot be grown. To point out that measurements of J7 indeed do not allow drawing conclusions on the nucleation process we wrote: “In the context used here, J7 does not mean the formation rate of critical clusters but shows the appearance of small particles that already comprise of many molecules that have participated in early particle formation.” (p. 25835 lines 1- 4).

To further stress this point we repeated the restriction to 7 nm in Section 6, Summary and conclusions. With some modifications in the wording the text now reads: “From previous studies, we know that traces of H2SO4 in a range of 10E5 - 10E6 cm-3 are present in our system and H2SO4 might have acted as a nucleating agent also in the experiments described here. Nevertheless, volatile organic compounds were necessary for particles to reach diameters of 7 nm. As such basic principles of RO2 chemistry were suitable to explain the dynamic behavior of the chemical system including NPF”.

From these statements it should be clear that, from the results shown in the manuscript, we cannot extrapolate from 7 nm particles to smaller particles. We therefore also do not speculate about the rate limiting step for the formation of smaller particles or critical clusters. We hope that this is clear for every reader and leave the title as it is.

Comment 2: The major equation, Eq.(1) on Page 25838, is derived by assuming Y(RONO2)/Y(O3) is constant, but Y(RONO2)/Y(O3) is affected by NO level that

changes from 0.3 to 103.5 ppb during the experiments, so the basis for this assumption needs to be clarified.

Response: There seems to be a misunderstanding. The ratio Y(RONO2)/Y(O3) is ratio of the probabilities that either RONO2 or an O3 is formed in reaction 2. This is a branching ratio and therefore by definition independent of [NOx] (see e.g. MCM, such numbers are given as a single number). Please do not confuse with the ratio of yields of RONO2/O3 versus yields of permutation reaction products in reactions of RO2 + NO and RO2 + RO2, respectively. This ratio certainly depends on [NOx].

Comment 3: P25829, “In clean background air, where only small amounts of particulate matter exist, new particle formation (NPF) has been observed.” NPF has been frequently observed all over the world, even in polluted regions such as Beijing in China.

Response: Thanks for the hint. We changed this text passage accordingly. The new text passage now reads: New particle formation (NPF) has been frequently observed all over the world (Kulmala et al., 2004a), in clean background air (e.g. DalMaso et al., 2007) as well as in urban atmospheres (e.g. Betha et al., 2013) The references Kulmala 2004a et al. 2004 and Betha et al. 2013 were added to the reference list.

Comment 4: P25834, what is the size range of UCPC measurement? There are some overlaps in the size ranges of the UCPC measurements and SMPS measurements, do they compare well and which instrument was used for the overlapped size region? Also, is the UCPC measured number concentration corrected for size-dependent particle loss?

Response: Part of this remark is consistent to remarks No. 1 and No. 2 of referee #1 and we therefore added the necessary information in the text of the manuscript and on the new Section S7 of the supplement.

With respect to overlap of size ranges: If we spray-generate aerosols in our Large Aerosol Chamber with CMD = 100 nm and GSD = 1.8 - i.e. when no nucleation mode is present - number counts of CPC3022 and SMPS/CPC3022 agree within 5 % (M. Folkers, Diss. Universität Köln, 2002).

Comment 5: The treatment of isoprene: on P25838 it says “Although contributions of isoprene were always less than 10% they were always considered in summing up BVOC concentrations”; on P25839 it says “Because the isoprene contribution was less than 10% and fairly constant from experiment to experiment: : : the impact of isoprene was neglected: There are clear inconsistencies here. If the effect of isoprene is neglected, isoprene should not be included in the total BVOC.

Response: There is no inconsistency. For calculating the yield of particle mass formation from a given BVOC mix we consider all BVOC in the mix, including isoprene. However, isoprene in the BVOC mix suppresses new particle formation by suppressing OH concentrations (Kiendler-Scharr et al., 2009). The impact of isoprene on suppression of new particle formation leads to $\sim$ 10% – 20% lower rates of new particle formation in the mix used here compared to a same mix without isoprene. As the contribution of isoprene was constant during the whole measurement period, also suppression of new particle formation by isoprene should be quite constant over the whole period. Compared to the suppression of new particle formation by NOX (more than 2 orders of magnitude) the 10 – 20 % suppression due to the abundance of isoprene was negligible. For clarification we now mention that consideration / negligence of isoprene is with respect to different quantities. The text now reads:

“Because the isoprene contribution was less than 10% and fairly constant from experiment to experiment, the suppressing impact of isoprene on new particle formation (see Kiendler-Scharr et al., 2009) was low.”

Comment 6: P25839: “The first was a decrease of J7 with increasing NOx.” J7 is not shown in the figure.

Response: Thanks for the hint. The respective sentence was changed to: The first was a decrease of maximum particle number concentration with increasing NOx indicating

a decrease of J7 with increasing NOx.

Comment 7: P25840, what is “incremental mass yield”? Is it different from the conventional “mass yield”? Please define.

Response: As incremental mass yield we defined the slope of the maximum particle mass, PMMAX, in dependence of consumed BVOC. As this definition is explicitly given in Mentel et al. (2009) we extended the text only shorty. The text now reads: Incremental mass yields were determined as described in Mentel et al. (2009). The maximum particle mass measured during the respective experiments was determined from the maximum volume assuming a density of 1.2 g cm-3. Slopes of maximum particle mass concentrations as function of consumed BVOC mass were taken as incremental mass yields. A yield of 11.7 $\pm$ 2%, R2 = 0.81 was determined for the data.

Comment 8: P25841, from “To analyze SOA mass formation” to the end of this section, I am not following this section. What is PMMAX,meas? How does the equation derived, e.g., where is the parameter 0.117 from? And “as long as BNR > 10, PMMAX,norm was independent of NOx within the error margins of the data.” Do you mean “independent of BNR”?

Response: For clarification we rephrased the respective text. This text now reads:

To analyze SOA mass formation as function of BNR, the impact of variable [BVOC]0 had to be separated from impacts of [NOx]0. This was achieved by normalizing [BVOC]0 to 65 μg m-3. Normalization was conducted using the results from the linear regression analysis of data obtained without NOx addition which resulted in a mass yield of 0.117 (11.7% see above). Considering that more than 95% of the BVOC introduced into the reaction chamber were oxidized, PMMAX,norm was calculated as:

PMMAX,norm = PMMAX,meas + 0.117* (65-[BVOC]0) (2)

In Equation (2), PMMAX,meas is the maximum particle mass measured during individual experiments and PMMAX,norm is the particle mass that would have been obtained if [BVOC]0 would have been 65 μg m-3 during each of these experiment. PMMAX,norm is shown in Fig. 7 as a function of BNR. The normalized data show still some scatter. However, as long as BNR > 10, PMMAX,norm was independent of NOx within . . .

Comment 8a: Also it is obvious that there are data points outside the error margins rather than “within error margins”.

Response: The lines shown in the old and in the new Figure 7 indicate ± 1sigma standard deviation from the mean of the data without NOx addition. Assessment of data points with NOx addition being inside or outside of error margins depends on the confidence level chosen for the assessment. Looking at the reproducibility of measurements without NOx addition we assess ± 1 sigma deviation as too low to decide if other data points are significantly outside the error margins.

Comment 9: P25841, please specify “diffusion source”

Response: We refer to the respective literature. We added the sentence: Details of the diffusion source are given in Mentel et al. (2009) and in Heiden et al. (2003).

Comment 10: P25843, “Mechanisms of SOA formation from molecules much larger than monoterpenes may favor a RONO2 route and may differ from those discussed here for monoterpenes.” Lim and Ziemann studied C8-C15 alkanes, whose MW are not much higher than monoterpenes (e.g., a-pinene). Therefore, perhaps anthropogenic vs biogenic VOC is a better hypothesis for the difference.

Response: Thanks for the hint. The text was changed to: Mechanisms of SOA formation from molecules with structures and chemical behavior different from that of monoterpenes may favor the RONO2 route and may differ from those discussed here for monoterpenes.

Comment 11: P25846, “P(O3) is thus a linear measure of Reaction (R2) and therefore also a measure of the [RO2] which is withdrawn from the PRP channels.”, should it be “Reaction R2a”?

Response: Our answer is yes and no. On the one hand ozone is formed only in reaction R2a. On the other hand, RO2 is also removed from PRP channels in reaction R2b. As the ratio of reaction rates of R2a/R2b is fixed by Y(O3)/Y(RONO2), P(O3) is a linear measure for both reaction rates, that of reaction R2a and that of R2b and therewith also to that of R2a+R2b which is the rate of reaction R2. As stated in the manuscript, the sentence is correct and we therefore leave the text in the form as it is.

Comment 12: Table 1, it will be better to include [NO]0 in the table, so readers do not have to calculate [NO]0.

Response: [NOX]0 is now added in Table 1 as third column.

Comment 13: In Figure 3, there is sharp decrease of the number concentration for all three curves for 6<x<8, what is the cause for that?

Response: Thanks for the hint. For clarification the following sentence was added to the Figure legend: The sharp decrease of particle number concentration observable 6 – 8 h after inducing particle formation by OH production was caused by switching off the OH production and subsequent particle formation.

Comment 14: Figure 3, it would be good to include time trace of OH in this plot for comparison, since OH affects NPF, and [OH] varies by a factor of 2 even for [NO]0 < 30 as shown in Fig. 6. This is specifically related to Section 5.1.2.

Response: We tried to include OH data in Figure 3 but this made the figure unclear because 6 traces would be shown in parallel. We therefore left Figure 3 as it is. Instead we changed Figure 4 where the requested information is now given at one example. The bar indicating the start of new particle formation in the old Fig. 4 is exchanged now by the measured particle number concentration over the whole time period allowing direct comparison of increasing OH concentrations with increasing particle number concentrations.

Comment 15: In Fig. 6, coloring the points by [BVOC]0 would support the argument that “the scatter of OH is due to [BVOC]0”

Response: Full coloring will lead to an unclear figure. We therefore decided to color the figure according to three different classes of [BVOC]0. We hope that this makes the point raised here clear enough. Changes made with this respect are described in the figure caption Fig. 6 (see our response to comment no. 4 of referee #1, Figure caption Fig. 6).

Technical corrections

1. P25828, Line 26, add “,” after “compounds” Thanks, done

2. P25829, Line 3, add “,” after “matter” Thanks, done

3. P25829, Line 7, change “play a key role for” to “play a key role in” Thanks, done

4. P25838, Line 22, change “%” to “percent” Thanks, done

5. P25841, Line 7, change “as function” to “as a function” Thanks, done

6. P25842, Line 7, remove “already” Thanks, done

7. In References, the reference of Seinfeld and Pandis, note pages.

Response: Thanks for the hint. EKMA plots are indeed much better described in the textbook of Finlayson Pitts and Pitts and we therefore exchanged the reference Seinfeld and Pandis by the reference Finlayson-Pitts and Pitts. The reference now reads: Finlayson-Pitts, B. J., and Pitts, J. N.: Atmospheric chemistry: Fundamentals and experimental techniques. P. 611-618. Wiley-Interscience, New York, 1986. ISBN 0-471-88227-5

8. SI information, P5, Line 13, change “in” to “is” Thanks, done

9. SI information, P8, Line 8, change “linear” to “linearly” Exchanged at P.8, line 33. Thanks.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 25827, 2013.