We sincerely thank both reviewers for valuable and relevant feedback that challenged our interpretations and helped improve the manuscript. Below are the copied comments of the reviewer reports (Calibri, highlighted in yellow) and our corresponding answers (in black) and changes in the manuscript *(italic)*.

Anonymous Referee #1

Ahlberg et al. presented a study that examined the effect of seed aerosol surface area, composition and phase on SOA mass yield in an oxidation flow reactor. This paper is potentially useful to the SOA community. However, there are portions of the manuscripts that are vague and confusing, and they need to be addressed before the manuscript can be considered for publication.

Thank you for the comments and effort. With the answers below, we hope that we have clarified any vagueness and confusing parts.

Specific comments:

1. Page 3 line 26: Why was a mixture of VOCs instead of pure a-pinene or pure mxylene used in these experiments? Won't modeling condensational sinks be easier if single-component VOCs were used in the experiments? Different LVOCs will be lost to the reactor's walls at different rates. Hence, the condensation sinks, extent of yield under-estimation etc. discussed in this manuscript are really some average of the apinene and m-xylene SOA systems. There is no way to determine which SOA system is the main cause of this yield under-estimation.

Using a mixture was not important for the end results. The reason we choose this mixture instead of just one VOC is that it may resemble ambient conditions more (where both anthropogenic and biogenic SOA are present in a mixture). Further, we showed in a previous paper (Ahlberg et al., 2017) that the SOA formation from this VOC mixture can be represented with a model that assumes that the condensed phase is an ideal mixture (following Raoult's law). If we would have seen significant deviations from what can be expected from an ideal mixture in our previous work, perhaps our approach would have been different in the present study. Yes, the yield under-estimation is an average of the two SOA systems. But as it is a function of the condensation sink, this doesn't matter for our conclusions regarding the yields. The condensation sink is a measured quantity in most OFR experiments. Although two VOCs introduces more complexity, both VOCs chosen are well known SOA precursors. Also, the wall loss effect of single SOA precursor experiments is very complex to model in detail. Even from one single VOC the oxidation products consists a myriad of different molecules with a wide range of different pure liquid saturation vapour pressures, reactivity in the condensed phase and on the walls, and molecular diffusion coefficients. All these properties influence their wall losses in OFRs.

2. Page 3 line 29: Related to the previous comment, were the a-pinene and m-xylene present in equal quantities in the mixture used? The authors mentioned that the evaporation rate of the mixture decreased over time. Did the evaporation rates of a-pinene and m-xylene decrease at the same rates?

The VOC concentrations were pretty similar (5.2 and 6.7 ppb respectively). This is already stated in the last paragraph of section 2.1. The evaporation rates declined by 10 and 17 % during the second week of the weighing experiment. This was 14 days after the start of the weighing experiment. As stated in the manuscript, it is important to note, that the timescales during weighing are much longer than the time-scales of the SOA experiments.

3. Page 4 line 11: I suggest that the authors define "OH reactivity" here (instead of a few lines further down) in order for their sentence to be less confusing.

Agree. Moved the definition.

4. Page 4 line 21: “from a few to 10 % on a mass basis. . .” it would be use to provide a number instead of using the term “a few”.

Since we didn’t measure the losses it is hard to give numbers. But our main point is that we don’t care about particle losses at the inlet, and that we therefore can assume losses lower than 10%.

We changed the formulation to:

Particle losses depend on reactor settings and particle sizes, but are generally lower than 10 % on a mass basis (Martinsson et al., 2015; Karjalainen et al., 2016; Ortega et al., 2016; Palm et al., 2016).

5. Page 4 line 30: Please provide the reasoning behind drying the aerosols before measurements by the SMPS and AMS.

Drying of the aerosols before the measurements by the SMPS is generally seen as crucial since one otherwise measures wet particle sizes, which varies with RH. For the AMS, which measures chemically resolved particle mass, drying is recommended to reduce uncertainties in the collection efficiency. The particles may bounce less if they are wet and also, the inlet losses are a function of size which may depend on the RH.

6. Page 6 line 11: How do the authors know that 100 % of the input VOCs will react in the flow reactor? VOC measurements? Modeling? It is worth explaining in the paper even though knowing the exact concentration of reacted VOC is likely not essential to the authors’ comparison of relative increase in mass yields.

This was calculated from the calibrated OH exposure and tabulated reaction rates of the VOCs. OH exposure divided by time gives OH concentration if it is assumed that OH is stable throughout the reactor volume. This is a simplification, but Li et al. (2015) showed that this is not too far from the truth. Since the OH loss rate is also low at the inlet, OH concentration builds up very quickly. With our OH exposure (7e11 molecs cm^{-3} s), the concentration was 4.3e9 molecules cm^{-3}. This gives lifetimes for α-pinene and m-xylene of 4.3 and 16.2 seconds respectively. Compared to the residence time (160 s), this is very short. We clarified the manuscript as follows.

Old text: In the oxidizing environment of the reactor, 100 % of the input VOCs are expected to react.

New formulation: *Assuming constant OH concentration, with our settings the VOC lifetimes for reaction with OH are short compared to the residence time (4.3 and 16.2 seconds, for α-pinene and m-xylene respectively). Therefore we assume that all VOCs have reacted.*

7. Page 6 line 17: The discussion on the mass yield uncertainties is confusing. What do the authors mean by “However, this may give a too small range”? Also, what do the authors mean by “No experiment was repeated fully”? I thought the authors replicated their experiments. Also, what do the authors mean by “. . ., but single point replicates gave a fractional error of 14 % compared to expected values”? What do these “expected values” refer to? In general, I highly recommend that the authors revise this discussion on mass yield uncertainties.

We agree that this was a bit confusing. We repeated the SOA only experiment twice per day. This is the most important test, since it is very sensitive to changes in OH exposure, VOC evaporation rate and flows. Also, this determines the VOC concentration during the full experiment and consequently the yields with seed particles. We have rewritten the paragraph to make it more clear.

Old text: The uncertainty in the yield increase was calculated from the standard deviation of the measurements. The fractional uncertainty was between 6-10 %. However, this may give a too small range. Although all flow, pressure, and OFR settings were checked, a variation larger than the experiment standard deviation is expected since the setup was highly sensitive to small perturbations. No experiment was repeated fully, but single point replicates gave a fractional error of 14 % compared to expected values. Therefore, a conservative expected repeatability of the experiments is within 20 %.

New text: *The uncertainty in the yield increase was calculated from error propagation of the standard deviations of the measurements. The fractional uncertainty with this method was between 6-10 %. However, this only reflects the precision in one experiment. Although all flow, pressure, and OFR settings were checked repeatedly, a variation larger than single experiment standard deviation is expected since the setup was highly sensitive to small perturbations. No experiment was* *repeated fully, but SOA levels without seeds was tested twice per day. Replicates of SOA yield with seeds gave a fractional error of 14 % compared to previous values. Therefore, a conservative expected repeatability of the experiments is within 20 %.*

8. Page 6 line 24: The authors used the expression "error in the yields of these experiments". This use of this expression feels inappropriate since it gives readers an initial impression that errors were made in the calculation of the yields, which is not the intention of the authors. I suggest using the expression "extent of yield under-estimation" instead.

Fixed. The sentence now reads:

The extent of yield underestimation in these experiments can be calculated by normalizing the yield increase with the maximum yield increase.

9. Page 6 line 27: What do the authors mean by "the produced organic sink"?

It is the contribution of SOA to the CS. We modified the sentence to:

Also seen in Fig. 4 is the modeled bias (fraction condensed on particles), following a similar trend but slightly lower since the experimental data only considers the condensation sink of the seed particles, while in the model the total sink (seed + SOA) is taken into account.

10. Page 6 line 28: How was the condensation sink calculated?

The condensation sink was calculated as in Pirjola et al. (1999). For this calculation, we made assumptions of the diffusion and mass accommodation coefficients following Palm et al. (2016). The diffusion coefficient was 7e-6 m^2 s^{-1} based on an oxidized 200 g mol^{-1} (Tang et al., 2015) molecule and the accommodation coefficient was set to 1 (Julin et al., 2014). See also answers to referee #2. The following was added to the manuscript:

Section 2.2: *For model sensitivity tests and uncertainties, the reader is referred to the original paper.*

11. Page 6 line 31: The authors stated "This could be due to increased particle losses in the reactor. . .". Is this explanation valid given that the authors stated that particle losses are small in section 2?

You are right that this looks contradictory. And even though losses of 10% could affect the curves, the losses shouldn't change much since the particle sizes will remain pretty much the same. Instead it is more likely that it could be due to the SOA being spread out on more particles which could increase heterogeneous oxidation that leads to fragmentation. But we don't want to speculate too much on this difference since it is not so pronounced. The manuscript was changed as follows:

Old text: However, while the LVOC model yield continues to increase with increased seed area concentration, the increase in the experimental yields levels off. This could be due to increased particle losses inside the reactor, which have not been considered.

New text: However, while the LVOC model yield continues to increase with increased seed area concentration, the increase in the experimental yields levels off. *This could be due to increased fragmentation losses from heterogeneous oxidation, since a larger portion of the SOA will be exposed with higher seed particle concentration.*

12. Fig 4: The y-axis is given as "Yield/Max yield" while the main text states that the y-axis is Yield increase/Max yield increase. Which is the correct y axis label?

This is actually the same thing (yield increase is the ratio of yield to SOA only yield and taking two yield increase ratios the SOA only yield is deleted). To keep it simple and avoid confusion we deleted "increase" in the text.

New text: *The extent of yield underestimation in these experiments can be calculated by normalizing the yield with the maximum yield.*

13. Page 7 line 16: The authors stated "At 10 ug/m3, the increase in yield is estimated from the linear regression between data points in Fig. 5. . .". This sentence is confusing. Which data points are the authors referring to? Do the authors fit all the data points for each VOC or only a subset of points near 10 ug/m3 OA? Why was linear regression used? Perhaps a

non-logarithmic version of Fig. 5 should be provided because the current figure looks like it is better fitted to an exponential function.

Since we don’t have data for exactly 10 ug/m3, we estimate it by simply taking two adjacent points and drawing a line between them. Yes, the full range of the data is better with fitted with other methods, but doing this would be unnecessary for this exercise which is a rough estimate

We changed the phrasing to:

At 10 µg m-3 the increase in yield is estimated, from linear regression between adjacent datapoints in Fig. 5, at 67 %, 80 %, 24 % and 94 % for α-pinene, m-xylene, myrcene and isoprene respectively

14. Page 7 line 20: What do the authors mean by “a higher VOC produces a sink faster than a low input”? Are they referring to the condensation sink rate? Also, won’t a higher VOC input result in higher concentrations of LVOC, some of which will be lost to the reactor’s walls? Also, pervious environmental chamber studies have shown that the use of different VOC concentrations may result in different peroxy radical chemistry and hence different SOA mass yields. Did the authors consider this possibility in their flow reactor study?

We are referring to the condensation sink, yes. Given that the OH concentration is not affected, a high concentration of VOCs would produce a certain amount of SOA faster than a low concentration. No, we did not consider the peroxy radical chemistry. A recent paper (Peng et al., 2019) discusses this issue in OFRs, but we don’t it is necessary to include this in the present manuscript since the VOC concentration was kept constant in all experiments.

The text was clarified as follows:

…since higher VOC concentrations also produce a condensation sink faster than a low input VOC concentration

15. Page 8 line 22: Do the authors mean “SOA mass fraction per particle”?

Yes. Modified the text as per suggestion.

16. Page 8 line 25: Kroll and co-authors studied the heterogeneous OH photooxidation of low-volatile organic aerosols such as squalane, oleic acid, linoleic acid etc., not SOA. Please make the appropriate revisions.

Thanks for noting this mistake. We changed “SOA” to “organic particles.”

17. Have the authors looked at how the oxidation state changes as a function of SOA mass concentration? This analysis may provide some insights into the possibility that particle-phase chemistry may be the reason for the increase in O/C with SOA mass concentration.

Yes, but since H:C is within such a small range, and OSc=2*O:C-H:C, it doesn’t add information that is not already in the van Krevelen diagram.

18. Although this is likely the first study that examine the effect of seed aerosols on SOA formation in a flow reactor, the effect of seed aerosols on SOA formation in chamber experiments has been studied by Huang et al. (JGR: Atmospheres, 2016). In that study, the authors performed PMF analysis on their data to determine that differences in particle-phase chemistry contributed to the differences in SOA mass yields when different seed aerosols were used in a-pinene ozonolysis experiments. Perhaps the authors can perform similar PMF analysis to their data to explain their results in this flow reactor study.

The suggestion to perform positive matrix factorization (PMF) on the recorded mass spectra is intriguing. However, it falls beyond the scope of the present study. The operational principle of PMF is that is exploits co-variance between measured variables between samples to construct static “building blocks” of the measured signal (factors), with varying abundance between samples. As applied to aerosol mass spectrometry, this means one reconstructs the measured ion time series by different combinations of factor mass spectra. This is readily done on dynamic data such as ambient measurement, or as for Huang et al, batch mode oxidation experiments (where an aerosol is continually measured in real time as it undergoes physicochemical transformation). OFR experiments of the type reported here are fundamentally different as the temporal variability is under the detailed control of the experimentalist; one changes set points as steady state and sufficient counting statistics are obtained. Therefore, PMF cannot be used in the conventional manner for our dataset.

Anonymous Referee #2

Ahlberg et al. investigated the yield of secondary organic aerosol (SOA) generated from the photooxidation of an m-xylene/⍰-pinene mixture in an oxidation flow reactor (OFR) as a function of seed particle surface area, type, and phase. At the operating conditions that were used, they found that the SOA yield increased by a factor of 2-3.5 as a function of increasing seed concentration from 0 to 3000 um2 cm-3 (condensation sink = 0 to 0.1 s-1), with the highest increases observed in the presence of ammonium nitrate and wet ammonium sulfate seeds. The seed dependence on SOA yield was modeled using the "LVOC fate correction" model published by Palm et al., ACP, 2016, and hypothesized to be due to residence-time-limited condensation of oxidation products in the OFR. The effect of SOA elemental ratios (H:C and O:C) was also characterized as a function of seed particle concentration. Given the emergence of OFRs as a technique to characterize SOA formation, and the previously established dependence of SOA yields on available condensation sink, I would support publication of this manuscript in ACP after consideration of my comments below.

Thank you for the comments and effort.

1. Somewhere in the manuscript, perhaps in conclusions, the authors should add a paragraph to discuss recommendations for (i) seed particle composition and (ii) seed particle surface area concentration for SOA yield measurements in OFR studies. For example:
    a. Should ammonium nitrate seeds be used because ammonium nitrate is less humiditydependent than ammonium sulfate? Are there deficiencies with using either AN or AS that could be addressed with other seed types?

We don't believe AN is less humidity-dependent than AS in terms of growth factor. However, efflorescence is not observed in AN which will affect the results depending on RH and seed particle drying. The second paragraph of the conclusions addresses this point, and includes recommendations for future studies on this issue.

    b. It seems that CS > 0.06 – 0.07 s-1 is required at the conditions that were used in these studies (e.g. PAM, 160 sec residence time). It would be useful to model or parameterize the CS that is required, as a function of residence time, in graphical or equation form.
    c. The work would have greater impact if the result can be generalized to other OFR designs that might for example have different surface-to-volume ratio than the PAM reactor and consequently different CS required to promote condensation.

Both of these are very good points that we tried to implement in a simplified manner. However, it is not easy to represent all different conditions and interdependent variables in neither graphical or equation form. E.g. the coefficient of eddy diffusion, k_e, used to calculate the wall loss, is dependent on reactor volume. But several different reactor designs could have the same volume but with different surface to volume (A/V) ratios, so a graphical representation of CS needed as a function of surface to volume and residence time would need assumptions of the relationship between radius and length, which is precisely the variables that are altered for different designs. Further, a representation of CS needed as a function of residence time would need to assume constant OH exposure or constant UV lamp power (actinic flux). Both of these are usually changed between different experiments (OH exposure follows the residence time if lamp power is constant). So, a generalization could be made if we make assumptions of certain variables, but this could be seen as an oversimplification that would not benefit the

OFR community. It could introduce more confusion and we strongly encourage each group to model their specific settings for each experiment. The following changes in the manuscript have been made:

Old text: The yield increase leveled off at a dry seed particle condensation sink of ~0.05 s^{-1} corresponding to a surface area concentration of ~1600 μm^2 cm^{-3}. This implies that it is crucial that the condensation sink is accounted for in OFR experiments where the absolute SOA mass is of interest.

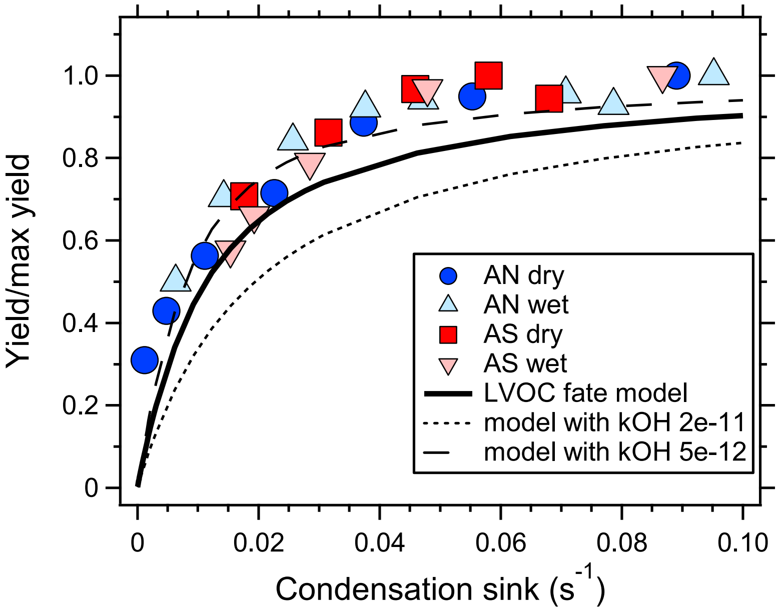
Now reads: *The yield increase leveled off at a dry seed particle condensation sink of ~0.05* s^{-1} *corresponding to a surface area concentration of ~1600* μm^2 cm^{-3}*. This value will be different for different reactor geometries and settings (such as OH exposure and residence time) and implies that it is crucial that the condensation sink is evaluated in all OFR experiments where the absolute SOA mass is of interest.*

2. I think it would be better to plot Figure 2 later in the paper so that the fractional LVOC loss pathways for the data points shown in Fig. 3 can be added to Figure 2.

If we understand correctly, this is what is shown in figure 4 where we combined model and data.

Additionally, the justification for assuming an OH reaction rate of 1E-11 cm3/molec/sec is never provided; thus, the associated level of uncertainty in the modeling is unclear. At the very least the model should be run over a wider range of OH rate constants—perhaps a factor of 2 or 5 in either direction relative to 1E-11 –to evaluate the sensitivity of the model result to the specified kOH.

The rate constant was taken from the original model in (Palm et al., 2016), where they assumed an oxygenated molecule with 10 carbon atoms and no carbon double bonds and took values from (Ziemann and Atkinson, 2012). In the alternative version of figure 4 shown below we added modelled SOA yield for rate constants of 2e-11 and 0.5e-11 cm^3 $molecs^{-1}$ s^{-1}.



As can be seen, the graphical agreement between measurements and model can be improved by using a slower rate constant. This could however be for the wrong reason. First of all, the datapoints are normalized to the maximum yield so they reach the value of one, which is not the case for the model which reaches ~0.9 condensed fraction at the maximum CS used. Also, the model takes into account any CS, while the data only used the seed CS. The purpose of the original figure was to show the similarities of the model and all measurements when they are normalized.

Using just one rate constant is of course a simplification, but from the sensitivity analysis that was done by Palm et al. (2016) the conclusion was that the model is more sensitive to other parameters, namely the sticking coefficient, the condensation sink and the average residence time. Therefore, we don't wish to publish the above figure, and instead the reader should refer to the original model. We modified the caption of figure 2 as follows:

Old text: Figure 2. The fractional fate of LVOCs as a function of particle surface area concentration, using the model of Palm *et al.* (2016). A molecule is assumed to fragment after reacting with OH five times. OH reaction rate was 1 x 10^{-11} cm^3 $molecs^{-1}$ s^{-1}. For reactor settings, see text.

Now reads: *Figure 2. The fractional fate of LVOCs as a function of particle surface area concentration, using the model of Palm et al. (2016), with the same OH reaction rate (1 x* 10^{-11} cm^3 $molecs^{-1}$ s^{-1}*) and assuming fragmentation after reaction with OH five times. For reactor settings, see text.*

3. I prefer that the authors not refer to their operating conditions as "atmospherically relevant." It's already implied that atmospherically relevant conditions were used, but the reader can decide the atmospheric relevance themselves in the context of specific atmospheric conditions or source regions. In the instances below, for example, it may not be generally true that RH = 60%, ORG = 5 ug/m3 are always "atmospherically relevant" conditions:

We agree.

a. "using an oxidation flow reactor operated at an atmospherically relevant RH of 60 %" (P1, L12-L13)

Deleted "atmospherically relevant."

b. "A relatively low, and atmospherically relevant, SOA mass concentration of ~5 µg m-3" (P3, L27)

Deleted "atmospherically relevant."

c. "liquid-liquid phase separation rarely occur at O:C ratios higher than 0.7 in systems containing atmospherically relevant organics" (P8, L9-L10)

Deleted "atmospherically relevant."

4. Introduction, and elsewhere as appropriate: Jathar et al., ES&T, 2017 and Zhao et al., ES&T, 2018 should be cited and discussed as their work also investigated SOA yield dependence as a function of particle concentration / condensation sink.

We have added these references at the following places:

Introduction: *Due to the fast processing in flow reactors, several studies have discussed the potential problem with low condensation sinks resulting in lower yields (Lambe et al., 2015; Palm et al., 2016; Ahlberg et al., 2017; Jathar et al., 2017; Simonen et al., 2017; Zhao et al., 2018).*

Section 3*: In all experiments the yield increased significantly with seed particle surface area, confirming previous findings (Lambe et al., 2015; Palm et al., 2016; Ahlberg et al., 2017; Jathar et al., 2017; Zhao et al., 2018).*

5. P1, L18: "low volatile" → "low volatility"

Changed.

6. P2, L24: I suggest adding "the yields of SOA generated from m-xylene…" or similar.

Old text: In similar studies the yields of m-xylene…

Now reads: *In similar studies the SOA yields of m-xylene…*

7. P3, L28: Please show a representative subset of SMPS & AMS size distributions of the seed/SOA mixtures as a function of seed concentration. How much of the SOA condenses on the seeds and how much homogenously nucleates to form new particles? This is not clear at present. The size distributions could be shown in the supplement.

The nucleation mode clearly disappeared after adding a certain amount of seed particles. We agree that we should show this in the manuscript. We did not make use of the AMS pToF data. The following figure and caption was added to the supplement:

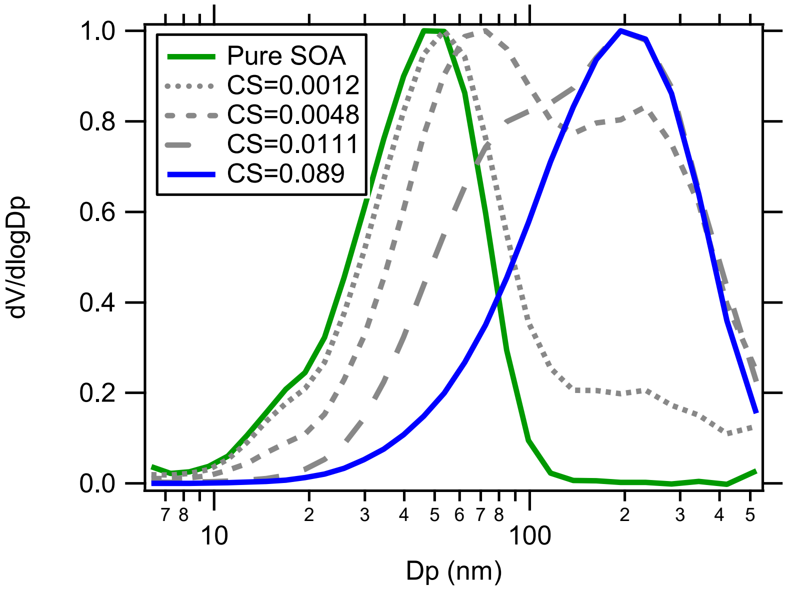


Figure S2. Example of how the volume size distribution changed during and experiment, from purely nucleated particles consisting of only SOA, through a mixture of nucleated and seed particles, to purely seed particles with condensed organics. Y axis is normalized so the differences in Dp are more clear.

The manuscript was modified as follows (section 2.4):

An example of the volume size distributions during an experiment is shown in figure S2.

8. P5, L6: The authors state: "Before experiments, the reactor was run without seeds or VOCs until the volume concentration was below 0.2 µm3 cm-3". Please clarify whether the lights were turned on for generating OH/O3 during these periods?

The sentence now reads:

Before experiments, the reactor was run *with the lamps on* without seeds or VOCs until the volume concentration was below 0.2 µm3 cm-3, as measured by the SMPS.

9. P6, L5: What is the mass-/volume-weighted mobility diameter? (possibly the more critical value in assessing how much of the mass is not transmitted through the AMS inlet lens?)

This is answered by the figure we added in comment nr 7 (fig. S2). The manuscript (section 2.4) was modified as follows (italic):

The relatively low CE of SOA may not only be a bounce effect, since these particles were significantly smaller, with a number mode around 20 nm*, and a volume mode around 40-50 nm in mobility diameter*, which to a higher degree are lost in the aerodynamic lens inlet of the AMS.

10. P7, L1-2: This statement is not clear: "which is similar the residence time of the reactor shortcircuit"

In some reactors, a short circuit bypasses the rest of the reactor. Material travelling through this way will have a significantly shorter residence time. This has been seen in for the PAM OFR in the references stated in the manuscript. The flow pattern in the PAM OFR was recently explored in more detail in Mitroo et al. (2018).

11. P8, L9: problem with citation formatting.

Actually, we don't see this…

12. P8, L20-L24: The authors state: “The O:C value increases with increasing SOA mass concentration (and seed particle concentration since these are connected), which is opposite to what is expected since more oxidized molecules tend to be less volatile (Shilling et al. 2009).[…] Increasing the seed particle number concentration also decreases the SOA mass fraction. It follows that SOA mass then is spread out on more particles, leaving less organics per particle, which could enhance the partitioning of more volatile material to the gas phase. This would leave more time for gas phase oxidation, and consequently a higher O:C ratio, provided the molecules partition to the particles.” There are a lot of nuances to this discussion. At the least, it is unclear whether the logic that is presented here is fully supported by the measurements. It also seems self-contradictory-for example, how can higher seed particle concentrations promote condensation of oxidized organic vapors (the main result of the paper) while simultaneously “[enhancing] the portioning of more volatile material to the gas phase”? These statements need to be reevaluated and modified in order to provide a more cohesive interpretation of the data.

We agree that this discussion is a bit speculative and unclear. Although one could imagine the same SOA yield despite more oxidation, it is contradictory to assume a larger evaporation rate and larger SOA yield simultaneously. It is more likely that it is the effect discussed in answers to referee #1 comment 11: A larger SOA area is exposed to heterogeneous oxidation with higher seed particle number concentrations.

We changed the paragraph as follows.

Old text: A more likely explanation to the change in O:C with SOA mass is the dynamics of the reactor. In these experiments, larger SOA concentrations are due to increased seed particle concentration. Increasing the seed particle number concentration also decreases the SOA mass fraction. It follows that SOA mass then is spread out on more particles, leaving less organics per particle, which could enhance the partitioning of more volatile material to the gas phase. This would leave more time for gas phase oxidation, and consequently a higher O:C ratio, provided the molecules partition to the particles. The higher O:C of wet AS could be explained if there are differences in heterogeneous chemistry. Kroll et al. (2015) showed that heterogeneous OH oxidation of SOA may increase the carbon oxidation state, on the expense of SOA mass.

New text: *A more likely explanation to the change in O:C with SOA mass is heterogeneous oxidation. Increasing the seed particle number concentration also decreases the SOA mass fraction per particle. It follows that SOA mass then is spread out on more particles, leaving less organics per particle, which enhances the area exposed to oxidation. Kroll et al. (2015) showed that heterogeneous OH oxidation of organic particles may increase the carbon oxidation state, however on the expense of SOA mass.*

13. Figure 3-4 and 6 should indicate the SOA precursors that were used (aPinene + m-Xylene), preferably in the figure axis labels or captions or both.

This has been added in the captions that now read as follows:

Figure 3. The increase in SOA yield from a mixture of m-xylene and α-pinene at different dry salt seed surface areas, normalized to the yield from experiments with no seed particles….

Figure 4. SOA yield increase, from a mixture of m-xylene and α-pinene, normalized by the maximum SOA yield increase and plotted against the dried seed particle condensation sink.

Figure 6. Van Krevelen diagram showing the elemental ratios of SOA from a mixture of m-xylene and α-pinene, with different seed particles.

14. Figure 4: what are the propagated uncertainties in yield ratios, condensation sink and in LVOC fate model outputs?

We added the propagated uncertainties (1σ) in yield ratios to the figure. CS std are the same as in figure 3 and smaller than the markers. As for the LVOC fate model, we have not calculated the uncertainties, and think that it is beyond the scope of this paper. The original model paper (Palm et al., 2016) and also Simonen et al. (2017) tested the model by oxidizing SO_2. The following changes to the manuscript were made:

Section 2.2: *For model sensitivity tests and uncertainties, the reader is referred to the original paper.*

Figure 4 and caption:

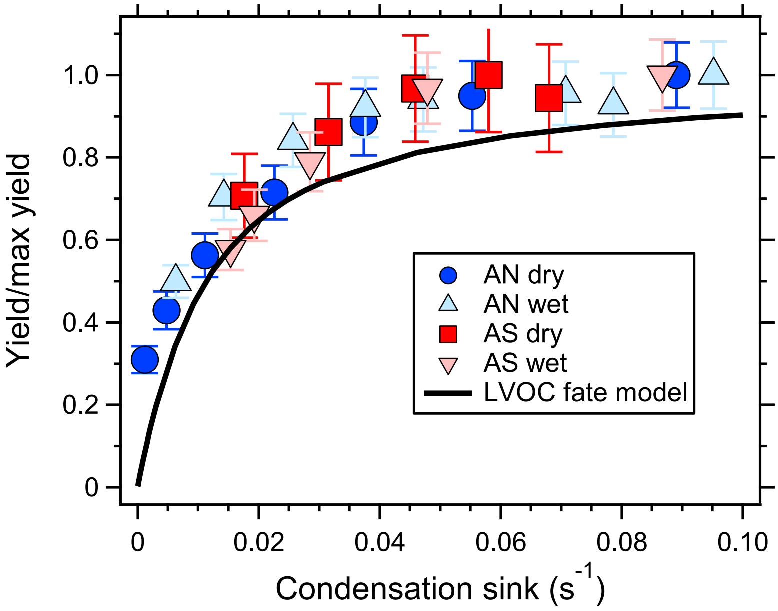


Figure 4. SOA yield increase, from a mixture of m-xylene and α-pinene, normalized by the maximum SOA yield increase and plotted against the dried seed particle condensation sink. Error bars denote the propagated uncertainties (1 std). The black line shows the fraction of condensed LVOCs according the model of Palm et al. (2016).

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Effect of salt seed particle surface area, composition and phase on secondary organic aerosol mass yields in oxidation flow reactors

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Abstract. Atmospheric particulate water is ubiquitous, affecting particle transport and uptake of gases. Yet, research on the effect of water on secondary organic aerosol (SOA) mass yields is not consistent. In this study the SOA mass yields of an α-pinene and m-xylene mixture, at a concentration of 60 µg m^{-3}, was examined using an oxidation flow reactor operated at an ~~atmospherically relevant~~ RH of 60 % and a residence time of 160 s. Wet or dried ammonium sulphate and ammonium nitrate seed particles were used. By varying the amount of seed particle surface area, the underestimation of SOA formation induced by the short residence time in flow reactors was confirmed. Starting at a SOA mass concentration of ~5 µg m^{-3}, the maximum yield increased a factor ~2 with dry seed particles, and on average a factor 3.2 with wet seed particles. Hence, wet particles increased the SOA mass yield by ~60 % compared to the dry experiment. Maximum yield in the reactor was achieved using a surface area concentration of ~1600 µm^2 cm^{-3}. This corresponded to a condensational lifetime of 20 s for low ~~volatile~~volatility organics. The O:C ratio of SOA on wet ammonium sulphate was significantly higher than when using ammonium nitrate or dry ammonium sulphate seed particles, probably due to differences in heterogeneous chemistry.

1. Introduction

The atmospheric aerosol is a dynamic mixture of organic and inorganic species. A large fraction of the organic aerosol is formed as a result of atmospheric processing of volatile organic compounds (VOCs), with products condensing onto pre-existing particles, forming secondary organic aerosol (SOA) (Hallquist et al., 2009). The partitioning of semivolatile organic species from gas to particles can be either adsorptive or absorptive depending on the chemical composition and phase of the particles (Pankow, 1994). Despite the complexity of the atmospheric aerosol, SOA mass yields (mass of formed particles divided by the mass of VOCs reacted) have traditionally been parameterized in models using simplified and relatively dry laboratory experiments.

Although not always measured, water is ubiquitous in the atmospheric aerosol, influencing particle size, scattering, transportation/deposition and uptake of gases, ultimately affecting both climate and health effects of particles (Pilinis et al., 1989; Nguyen et al., 2016). The aerosol liquid water content at subsaturation of water vapour depends on the relative humidity (RH), dry particle chemical composition and size. The most abundant inorganic aerosol compounds in submicron aerosol particles are the salts ammonium sulphate (AS) and ammonium nitrate (AN), which are mostly of anthropogenic origin (e.g. Poschl, 2005; Zhang et al., 2007). A portion of the water in particles can be regarded as anthropogenic water since both nitrate and sulphate generally increase particle hygroscopicity (Carlton and Turpin, 2013; Hodas et al., 2014), which in turn facilitates SOA formation of water soluble organic compounds. This particle formation pathway is believed to be especially important for isoprene SOA, since isoprene's first generation oxidation products are relatively small molecules with high saturation vapour pressures compared to the oxidation products of other common SOA precursors (Carlton et al., 2009; Ervens et al., 2011; Sareen et al., 2017). Also, the electrolyte solution of ammonium sulphate and ammonium nitrate is acidic since ammonia is a weak base, which increases the reactive uptake of several SOA species (Jang et al., 2002; Gao et al., 2004).

SOA research has been substantial during the last two decades, and the effects of relative humidity and aerosol liquid water on particle yields have been investigated in numerous studies. From partitioning theory it can be shown (Seinfeld et al., 2001; Hallquist et al., 2009; Pankow, 2010) that there should be a clear SOA mass yield dependence with RH, especially at low precursor concentrations, if an activity coefficient of 1 is assumed. Hennigan *et al.* (2008) showed that in an urban region dominated by biogenic emissions, partitioning to liquid water may be a significant contributor to SOA mass. However, adding water to laboratory oxidation experiments complicates the interpretation, since both gas (Jonsson et al., 2006; Warren et al., 2009) and particle phase (Ervens et al., 2011) chemistry may change. Furthermore, the yield variation with different RH can be NOx dependent (Ervens et al., 2011). For isoprene, both particulate water and acidity is believed to have strong effects on the SOA yield (Surratt et al., 2007; Carlton et al., 2009). Wong et al. ~~(2015)~~(2015) showed that wet ammonium sulphate seed particles resulted in 60 % more isoprene SOA being formed compared to a system with dry seed particles at the same RH. However, laboratory studies using other SOA precursors are somewhat inconsistent. Prisle *et al.* (2010) saw no influence of RH (up to near 100 %) on α-pinene ozonolysis SOA yields with ammonium sulphate seeds. Cocker III *et al.* (2001a), investigating the same system, but using dry or wet seed particles found that mass yields varied little with RH but decreased if the seed particles were wet. In similar studies the SOA yields of m-xylene, 1,3,5-trimethylbenzene (Cocker et al., 2001b) and toluene (Edney et al., 2000) have been found to be unaffected by the aerosol liquid water content. Lu *et al.* (2009) found no effect on m-xylene SOA yields with wet or dry neutral seed particles, while the yield was increased with dry acidic seed particles. In contrast, other studies have found that higher RH significantly increases the SOA mass yield of toluene and xylenes (Kamens et al., 2011; Zhou et al., 2011). Also, more recently, Stirnweis *et al.* (2017) assessed the influence of NOx and RH on α-pinene SOA with different seed particles and concluded that particulate water significantly increases the organic mass yields. Further, Faust et al. ~~(2017)~~(2017) found 13 and 19 % increases in SOA yield from α-pinene and toluene respectively, when SOA was formed on wet salt particles. It can be difficult to compare the results of different SOA oxidation experiments, since the conditions used are rarely the same. SOA yields can depend on e.g. temperature, NOx concentrations, precursor concentration, oxidant exposure and type, seed particle concentration and composition.

In the following work we report SOA yields from a mixture of α-pinene and m-xylene oxidized in a PAM oxidation flow reactor (OFR) (Kang et al., 2007; Lambe et al., 2011a), in the presence of wet or dry ammonium sulphate and ammonium nitrate seed particles. In contrast to many other studies looking into the effect of particulate water on SOA mass yields, the RH was held constant at 60 %, while the seed particles were either dried below an RH of 10 % or kept in their droplet state. Previous studies have shown that SOA produced in the reactor is similar to that produced in traditionally used smog chambers (Bruns et al., 2015; Lambe et al., 2015). The reactor can produce a more oxidized aerosol, which is strongly linked to the hygroscopicity of organic aerosols (Pang et al., 2006; Chang et al., 2010; Lambe et al., 2011b). Due to the fast processing in flow reactors, several studies have discussed the potential problem with low condensation sinks resulting in lower yields (Lambe et al., 2015; Palm et al., 2016; Ahlberg et al., 2017; Jathar et al., 2017; Simonen et al., 2017; Zhao et al., 2018). This effect was systematically investigated during the course of the experiments by using different seed particle concentrations.

2. Methods

2.1 Experimental set-up

All experiments consisted of introducing a constant flow of SOA precursors with a varying concentration of seed particles into an oxidation flow reactor. The experimental set-up is shown in Fig. 1. Seed particles were formed from atomization of a ~1 g/l solution of ammonium sulphate (Sigma Aldrich, ≥99 %) or ammonium nitrate (Sigma Aldrich, ≥99.5 %) in molecular grade water. The size distribution of seed particles had a maximum volume concentration at a mobility diameter between ~150-200 nm. Although the molality of the solutions and pressure in the atomizer were similar in all experiments, the output number size distributions were not identical. The number of particles per volume unit, as measured by the SMPS increased in the following order: dry AS>wet AS>dry AN>wet AN. The RH in the reactor was chosen between the deliquescence and efflorescence points of ammonium sulphate (Seinfeld and Pandis, 2012) and sodium chloride (experiments not reported here due to instrument failure) so that the hysteresis effect could be used to alternate between aqueous and dry particles. Ammonium nitrate have a reported deliquescence RH of 61.8 % (Tang and Munkelwitz, 1993) but efflorescence is not observed (Svenningsson, 1997; Lightstone et al., 2000). Seed particle mass concentrations of ~0-100 µg m^{-3} were achieved by pulling a varying flow (0-0.7 lpm) from the atomizer through the reactor.

VOCs were introduced into the reactor using a diffusion system with thin capillaries, described in Ahlberg *et al.* (2017). VOCs were chosen to get a mix of biogenic (α-pinene) and anthropogenic (m-xylene) SOA. The flow of VOCs was held constant throughout an experiment. A relatively low~~, and atmospherically relevant,~~ SOA mass concentration of ~5 µg m^{-3} without seed particles was aimed for so that the nucleated particles would not be the dominant condensation sink. The VOC concentration was determined after the experiments by the liquid weight loss during four weeks. During these weeks, the evaporation rate declined, probably due to VOC oxidation or VOC condensation inside the capillaries. Therefore the values of the first weighing was used. If the decline during the first week, prior to the first weighing, was the same as consecutive weeks, it would result in an overestimation of 13 % in the summed yield. Since the timescales of an experiment (~8 h) was much shorter, oxidation or condensation inside capillaries is not expected to have taken place. The total concentration of VOCs at the reactor inlet was calculated to be 60 µg m^{-3} (5.2 ppb α-pinene and 6.7 ppb m-xylene), hence the SOA mass yield with no seeds was ~8 %, in agreement with previous measurements of the same mixture (Ahlberg et al., 2017), albeit at slightly different VOC ratios.

2.2 SOA formation

SOA was produced using a PAM oxidation flow reactor, which has been extensively used in laboratory and field measurements (https://sites.google.com/site/pamwiki/). The reactor, which is a 13.2 l horizontal aluminium cylinder with passivated walls, produces very high concentrations of ozone and hydroxyl radicals (OH) from UV lights mounted inside (Kang et al., 2007; Lambe et al., 2011a). In recent years measurements and modelling have significantly advanced the knowledge of the reactor and best practices during use have been developed (Ortega et al., 2013; Li et al., 2015; Peng et al., 2015; Palm et al., 2016; Peng et al., 2016). Briefly, the reactor should not be used with too high OH reactivity (defined as the concentration of reactant multiplied by the OH reaction rate) input, since OH may be suppressed. The same problem may arise if the OH exposure is low due to low lamp voltage or low absolute humidity. In this work the flow was set to 5 lpm and only one lamp was used. Lamp voltage was adjusted to reach an O_3 concentration of 2.7-3 ppm. RH in the reactor was held constant at 60 % by PID regulation of a humidified flow. With these settings the OH exposure, calibrated off-line using 10 ppb of SO_2 (for detailed procedure, see Lambe et al., 2011a), was 7 x 10^{11} molecules cm^{-3} s, with an experimental uncertainty (1σ) of 5 %. The total OH reactivity~~ (defined as the concentration of reactant multiplied by the OH reaction rate)~~ was 9.4 s^{-1} which is not believed to have induced significant OH suppression (Peng et al., 2015; Peng et al., 2016). The temperature increase inside the reactor due to the lamp was measured to 1-2°C prior to the experiments using a thermocouple inserted into the reactor. With an RH of 60 % at 22°C (room temperature), RH inside the reactor is expected to be 53 %, which is above the efflorescence point of ammonium sulphate at the same temperature.

Particle losses depend on reactor settings and particle sizes, but are generally ~~low; from a few up to~~lower than 10 % on a mass basis (Martinsson et al., 2015; Karjalainen et al., 2016; Ortega et al., 2016; Palm et al., 2016). Ortega *et al.* (2013) found that most of the particle losses takes place at the inlet of the reactor. In this work, losses at the inlet are not of importance, since we look at SOA formed inside the reactor only. Palm *et al.* ~~(2016)~~(2016) constructed a model for the fate of low volatile organic compounds (LVOCs) in the reactor, in which four loss terms are competing: condensation onto particles, wall loss, fragmentation (assumed after reacting with OH five times) and outflowing from the reactor. The model was compared with the SOA mass yields at different seed concentrations. For the reactor settings used, the modelled LVOC fate as a function of seed particle area is shown in Fig. 2. For model sensitivity tests and uncertainties, the reader is referred to the original paper.

2.3 Particle measurements

After oxidative ageing in the reactor, the aerosol was dried below 30 % RH before size distribution and mass based chemical composition was measured using a scanning mobility particle sizer (SMPS, Wiedensohler et al., 2012) and an Aerodyne high resolution time-of-flight aerosol mass spectrometer (AMS, DeCarlo et al., 2006), respectively. The SMPS consisted of a custom-built DMA and a TSI CPC (model 3010). Silica gel driers decreased the RH of the sheath flow to below 10 %. The DMA voltages were calibrated prior to experiments and the number size concentration was checked using PSL spheres. The AMS was calibrated using size selected ammonium nitrate and ammonium sulphate particles.

2.4 Experimental procedure and data analysis

An overview of the experiments can be seen in Table 1. Before experiments, the reactor was run with the lamps on without seeds or VOCs until the volume concentration was below 0.2 µm^3 cm^{-3}, as measured by the SMPS. Before adding VOCs, 2-5 concentration levels of pure seed particles were measured to be able to parameterize organic impurities from the atomizer as a function of salt concentration. Despite using ultrapure water and zero air (Linde, GT30000), up to 6 % of the total mass of the seed particles were organic impurities and scaled roughly in a linear way with salt ion concentration. Pieber *et al.* (2016) found interferences in the *m/z* 44 signal from reactions in the ionization region facilitated by inorganic salt particles. However, in our experiments the m/z 44 signal was only ~15 % of the total organic impurity signal. Before calculating SOA yields, the impurities were removed from the organic signal using the linear relationship with the salt ions. After adding a constant concentration of VOCs, SOA was measured at 5-8 different seed particle concentrations. For each seed type, experiments without seed particles were performed to get a base level yield. This level was relatively stable between experiments, at 5.0 ±0.5 µg m^{-3} (1σ). Using data from a similar mixture in Ahlberg *et al.* (2017) the difference in base level corresponds to a difference in VOC concentrations of ±2 µg m^{-3} (±3.3 %). During the dry ammonium nitrate experiment, the base level drifted from 5 µg m^{-3} at the start to 6 µg m^{-3} at the end of the day. For this experiment, a time adjusted base level was implemented. The adjustment translated to an increase in the SOA mass yield by at most 15 % for the lowest seed concentration, to 1 % at the highest seed concentration.

The SMPS was used to determine the particle number size distribution and total particle volume and area concentrations. To calculate the input dry seed particle surface area concentration, a parameterization from pure salt measurements was made as a function of either sulphate or nitrate concentration as measured by the AMS. The size distribution was also used to calculate the condensation sink (*CS*) (Pirjola et al., 1999). However, we use area concentration when presenting our data since this is a measurement more often used and in these experiments scaled linearly with *CS*.

AMS data was evaluated using standard AMS analysis programs (Squirrel v1.57 and Pika v1.16). Standard changes to the fragmentation table and high-resolution spectra were made, including corrections for zero air CO_2 concentrations and removal of organic peaks overlapping with either air or salt peaks (*m/z* 14, 16, 32, 48, 64 for AS and 14, 16, 30, 46 for AN). The ammonium nitrate calibration of the AMS was used to calculate the relative ionization efficiency (RIE) of ammonium, which was subsequently used to calculate the RIE of sulphate. The RIE of ammonium was 4, which is the default value of the AMS, but the RIE of sulphate, at 1.96, was significantly higher than the default value of 1.2. Although this means that the measured sulphate mass was decreased during analysis, it doesn't affect the seed area calculations since the parameterization and seed mass changes cancel each other. For organics, the default RIE of 1.4 was used. To evaluate the AMS collection efficiency (CE) of the different experiments, the volume concentration as measured by the SMPS was multiplied by particle density calculated from the AMS chemical composition. A density of 1.4 g cm^{-3} was used for SOA from previous parameterizations of a similar mixture (Ahlberg et al., 2017). The collection efficiencies used as a function of SOA mass fraction can be seen in Fig. S1. CE for pure salts are listed in Table 1. CE of both wet and dry ammonium sulphate increased with increasing SOA mass fraction, likely due to decreased bounce. For ammonium nitrate, CE was roughly constant around 1. Pure SOA had a CE of 0.63±0.03 (1σ). The relatively low CE of SOA may not only be a bounce effect, since these particles were significantly smaller, with a number mode around 20 nm, and a volume mode around 40-50 nm in mobility diameter, which to a higher degree are lost in the aerodynamic lens inlet of the AMS. An example of the volume size distributions during an experiment is shown in figure S2. The "improved ambient" parameterization was used to calculate elemental ratios (Canagaratna et al., 2015). However, the organic portion of the particles consisted of both SOA and salt impurities. To calculate the O:C and H:C ratios of SOA only, the elemental ratios of the impurities only and their fraction of the total organics were used. This correction increased SOA O:C by ~8 % and decreased H:C by ~0.5 % for AS while for AN the change in O:C was below 1 % and H:C decreased 1-2 %.

The SOA mass yield is defined as the amount of SOA formed divided by the amount of VOCs reacted. ~~In the oxidizing environment of the reactor, 100 % of the input VOCs are expected to react.~~Assuming constant OH concentration, with our settings the VOC lifetimes for reaction with OH are short compared to the residence time (4.3 and 16.2 seconds, for α-pinene and m-xylene respectively). Therefore we assume that all VOCs have reacted. However, comparing yields only would give a skewed result, since small differences in base SOA level between the experiments (Table 1) give large differences in yield. Instead we compared the ratio of base level SOA mass to SOA mass at different seed particle concentrations, which is equal to the relative increase in yield (unitless). This cancels out the VOC concentrations from the calculations. The uncertainty in the yield increase was calculated from error propagation of the standard ~~deviation~~deviations of the measurements. The fractional uncertainty with this method was between 6-10 %. However, this ~~may give a too small range.~~only reflects the precision in one experiment. Although all flow, pressure, and OFR settings were checked repeatedly, a variation larger than ~~the~~single experiment standard deviation is expected since the setup was highly sensitive to small perturbations. No experiment was repeated fully, but ~~single point replicates~~SOA levels without seeds was tested twice per day. Replicates of SOA yield with seeds gave a fractional error of 14 % compared to ~~expected~~previous values. Therefore, a conservative expected repeatability of the experiments is within 20 %.

3. Results and discussion

Figure 3 shows the increase in yield as a function of dry salt seed particle surface area concentration. In all experiments the yield increased significantly with seed particle surface area, confirming previous findings (Lambe et al., 2015; Palm et al., 2016; Ahlberg et al., 2017; Jathar et al., 2017; Zhao et al., 2018). The ~~error in the yields of~~extent of yield underestimation in these experiments can be calculated by normalizing the yield ~~increase~~ with the maximum yield~~ increase~~. Doing this, all experiments follow the same trend with seed surface area, seen in Fig. 4. Also seen in Fig. 4 is the modeled bias (fraction condensed on particles), following a similar trend but slightly lower since the experimental data only considers the condensation sink of the seed particles, while in the model the ~~produced organic~~total sink (seed + SOA) is ~~also~~ taken into account. The yield error decreases up to a condensation sink of ~0.05 s^{-1} corresponding to a seed surface area of ~1600 μm^2 cm^{-3}. Above this value, the LVOC fate model (Fig. 2) also indicates a slower increase. However, while the LVOC model yield continues to increase with increased seed area concentration, the increase in the experimental yields levels off. This could be due to increased ~~particle~~ fragmentation losses ~~inside~~from heterogeneous oxidation, since a larger portion of the ~~reactor, which have not been considered~~SOA will be exposed with higher seed particle concentration. The condensation sink at which the data levels off, corresponds to a lifetime (τ_{CS}) of 20 s, which is similar to the residence time of the reactor short-circuit (Lambe et al., 2011a; Ahlberg et al., 2017).

The results suggest that previous measurements using similar reactors have underestimated the yield at low condensation sinks. Because the error is larger at low yields, the yield curves will have a steeper increase and reach a constant yield at lower mass concentrations. Applying corrections to previous reactor experiments relying on nucleated particles as the only condensation sink is not trivial, since the condensation sink varies with time in the reactor. However, at a similar SOA condensation sink as that used in this study (0.022 s^{-1}), the yields should increase by a factor 2-3 compared to when no seed is used (Fig. 3). Given the shape of the yield bias in Fig. 4, at lower concentrations (and condensation sinks) the increase should be even higher. According to the LVOC fate model a 3-fold increase in yield (yield/max yield of 0.33) corresponds to a condensation sink of ~0.006 s^{-1}, suggesting the effective *CS* at this mass concentration is ~1/3 (0.006/0.022) of the reactor outlet *CS* in nucleation experiments. At half of that condensation sink (0.003 s^{-1}), the model predicts a 5-fold increase in yield, and at 1/10 (0.0006 s^{-1}) the increase could be as high as a factor 45. In Fig. 5 we used the LVOC fate model to recalculate the yields of Ahlberg *et al.* (2017). The inverse of the fraction condensed on particles at 1/3 of the experimental *CS* was multiplied with the measured yields and mass concentrations. Because both x and y values increase (both SOA mass and yields change with the same factor), the change from the measurements is not as dramatic as when only looking at the absolute yield increase or if yields were plotted against reacted VOCs. At 10 µg m^{-3} the increase in yield is estimated, from ~~the~~ linear regression between ~~the~~adjacent datapoints in Fig. 5, at 67 %, 80 %, 24 % and 94 % for α-pinene, m-xylene, myrcene and isoprene respectively, with the differences arising from differences in the size distribution of each SOA precursor. It is likely that our assumption that that the effective *CS* is 1/3 of the output underestimates the yield at low mass concentrations and overestimates the yield at high mass concentrations, since ~~a~~ higher VOC ~~input produces a~~concentrations also produce a condensation sink faster than a low input

VOC concentration. Although the calculations may be an oversimplification, it is clear that the SOA mass yields at low mass concentrations are biased low and that seed particles have a big impact in OFR experiments.

The second main result, also seen in Fig. 3, is that the increase in yield with increased seed concentration is lower for the dry ammonium sulphate experiment. Since ammonium nitrate does not effloresce (Svenningsson, 1997; Lightstone et al., 2000) it is likely that both wet and dry AN adjusted to the RH of the reactor and thus these experiments are essentially the same. Also, while the yield increase is highest for wet AS, this experiment had a lower base level SOA mass concentration, making it harder to rank the three wet experiments. The grey area in the figure represents ±20 % of the three experiments where the seed particles did not effloresce and is added to emphasize the similarities between them. Dry ammonium sulphate was the only crystalline particle, with a yield bias of a factor ~2, while the other three experiments were similar given the experimental uncertainty, with a yield bias factor of 2.9-3.5. Hence, wet seed particles increased the yield by 45-75 %, with an average of 60 %, compared to the dry seed experiment.

The difference between wet and dry experiments can be due to either differences in partitioning, reactive uptake or both. Julin *et al.* ~~(2014)~~(2014) showed that the mass accommodation coefficient of several different organic molecules is unity, regardless of the particle phase state. In their study, the condensed and gaseous phases consisted of the same molecules, which is not the case in the present study. However, as soon as a layer of organics has condensed on the crystalline AS particles, the mass accommodation for uptake at the surface should approach unity. If an aqueous phase is to increase the yield by equilibrium partitioning, the organic molecules need to be water soluble and SOA mass concentration needs to be low enough to retain an appreciable amount in the gas phase (Hallquist et al., 2009; Pankow, 2010). Several studies have shown that organic aerosol particles may undergo liquid-liquid phase separation (Song et al., 2012b; You et al., 2012; Zuend and Seinfeld, 2012). However, the water solubility of organic molecules increases with decreasing molecular weight and increasing polarity (O:C) (Varutbangkul et al., 2006; Massoli et al., 2010; Duplissy et al., 2011), both of which are favoured in OFR experiments compare to smog chambers. It has been shown (Song et al., 2012a, b) that liquid-liquid phase separation rarely occurs at O:C ratios higher than 0.7 in systems containing ~~atmospherically relevant~~ organics, water and AS. In the present study O:C was always higher than 0.7, which is seen in Fig. 6 that shows the elemental ratios in Van Krevelen space as measured by the AMS.

The elemental ratios of all experiments fall within a relatively narrow range (Fig. 6). The difference between wet and dry AN and dry AS is similar to the difference between pure SOA on different days (white symbols), with O:C within 0.83 ± 0.08 (1σ) and H:C within 1.33 ± 0.05 (1σ). The wet AS experiment however reaches higher O:C values and spans a larger range. The O:C value increases with increasing SOA mass concentration (and seed particle concentration since these are connected), which is the opposite to what is expected since more oxidized molecules tend to be less volatile ~~(Shilling et al., 2009)~~(Shilling et al., 2009). The increase is mostly due to the mass fragments with *m/z* 28 and 44. Several acid catalyzed oligomerization reactions change the elemental ratios of SOA, but with lower O:C as a result (Jang et al., 2002; Chen et al., 2011). Also, saturated AN and AS solutions have similar pH (4.5 and 4.2 respectively according to the E-AIM model (Clegg et al., 1998)), hence there should be no big difference between the wet experiments. A more likely explanation to the change in O:C with

SOA mass is ~~the dynamics of the reactor. In these experiments, larger SOA concentrations are due to increased seed particle concentration.~~heterogeneous oxidation. Increasing the seed particle number concentration also decreases the SOA mass fraction per particle. It follows that SOA mass then is spread out on more particles, leaving less organics per particle, which ~~could enhance the partitioning of more volatile material to the gas phase. This would leave more time for gas phase oxidation, and consequently a higher O:C ratio, provided the molecules partition to the particles. The higher O:C of wet AS could be explained if there are differences in heterogeneous chemistry.~~enhances the area exposed to oxidation. Kroll et al. (2015) showed that heterogeneous OH oxidation of ~~SOA~~organic particles may increase the carbon oxidation state, however on the expense of SOA mass. The water uptake (growth factor) of AN and AS are slightly different at 60 % RH, with an area increase of ~1.4 and ~1.7 respectively. However the O:C increase with increasing area is much larger for wet AS than for any other experiment, hence a chemical explanation is needed. To the best of our knowledge, there are no measurements on differences between OH radical uptake on different salt solution surfaces. Wang *et al.* ~~(2016)~~(2016) found that the salting out effect (pushing dissolved molecules out of the water phase) of several different organic molecules is stronger in sulphate compared to nitrate solutions. However, the compounds used were not similar to the SOA used in this study and this effect should cause opposite results since the yield increase is slightly higher for wet AS than for the AN experiments. Takami *et al.* (1998) showed that below a pH of 7 the uptake coefficient of OH increases with acidity. Given the small difference in acidity between saturated AN and AS it is uncertain if this can explain the measurements. Wick and Dang (2006) found that solvation of OH was correlated with increasing NaCl salt concentration. A possible pathway for differences in reactive uptake of OH between the salt solutions is the reaction with HSO_4^-, forming sulphate radicals (Jiang et al., 1992). Sulphate radicals have been shown to be an important source of organosulphates (Noziere et al., 2010; Schindelka et al., 2013). However, sulphate from organics is indistinguishable from inorganic sulphate in the AMS mass spectra since the fragmentation patterns are the same (Farmer et al., 2010), and thus should not affect the calculated O:C ratios. If sulphate aerosols affect the organic portion, this should be seen in ambient samples. Indeed, several studies have shown that the more oxidized SOA (LV-OOA) is correlated with sulphate (Ng et al., 2011b; Zhang et al., 2011; Crippa et al., 2013; Hao et al., 2014), but a more straightforward explanation to this is the fact that both are secondary aerosol constituents.

4. Conclusions

Experiments were conducted with two aims: (i) to investigate the influence of an aerosol liquid water phase on SOA yields and (ii) verifying and quantifying the underestimation of SOA production in oxidation flow reactors due to limited time for condensation. It was found that in all cases there was a strong increase in yield with increased seed surface area concentration, and that the yield with wet seed particles was 45-74 % higher compared to dry seed particles. The yield increase leveled off at a dry seed particle condensation sink of ~0.05 s^{-1} corresponding to a surface area concentration of ~1600 μm^2 cm^{-3}. ~~This~~This value will be different for different reactor geometries and settings (such as OH exposure and residence time) and implies that it is crucial that the condensation sink is ~~accounted for~~evaluated in all OFR experiments where the absolute SOA mass is of interest.

If seed particles are used to drive the partitioning to the particle phase, the choice of seed may affect the results due to differences in heterogeneous chemistry and water uptake. This makes translation of lab results to atmospheric relevance more difficult since a much higher seed particle concentration is needed in a reactor than in the atmosphere to make the condensed fractions comparable. To further study and parameterize the effects of the condensation sink on OFR SOA, future experiments should focus on different VOC concentrations with varying seed particle surface area, as well as using different seeds or seed mixtures.

Using dry ammonium sulphate seed particles the maximum yield increase was approximately a factor 2, while all wet experiments were similar and induced an increase above a factor 3. Hence, the wet particles produced around 60 % more SOA mass. The O:C ratio increased with decreasing SOA mass fraction. Also, O:C was higher with wet AS compared to other seeds, something which needs further research to fully explain, but is likely due to heterogeneous chemistry. These results point to the importance of anthropogenic water as an important source of SOA.

Data availability. Data are available upon request from the corresponding author.

Author Contributions. EA designed the study together with BS, performed the experiments, analyzed the data and prepared the manuscript with contributions from all coauthors. AE was responsible for AMS data quality assurance.

Competing interests. The authors declare that they have no conflict of interest.

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Table 1. For each of the four experiments the table shows dry seed surface area concentration, collection efficiency (CE) of the AMS for salts without SOA, initial SOA without seed particles (two replicates where available) and maximum SOA concentrations (with seed particles).

	Seed area range ($\mu m^2\ cm^{-3}$)	CE (1σ)	SOA initial ($\mu g\ m^{-3}$)	Max SOA ($\mu g\ m^{-3}$)
AS dry	570-2210	0.57 (0.05)	5.2, NA	10.6
AS wet	500-2820	0.76 (0.01)	4.5, 4.5	16.8
AN dry	40-2900	0.93 (0.04)	5.0, 5.9	22.0
AN wet	210-3090	1.02 (0.07)	5.0, 4.6	15.3

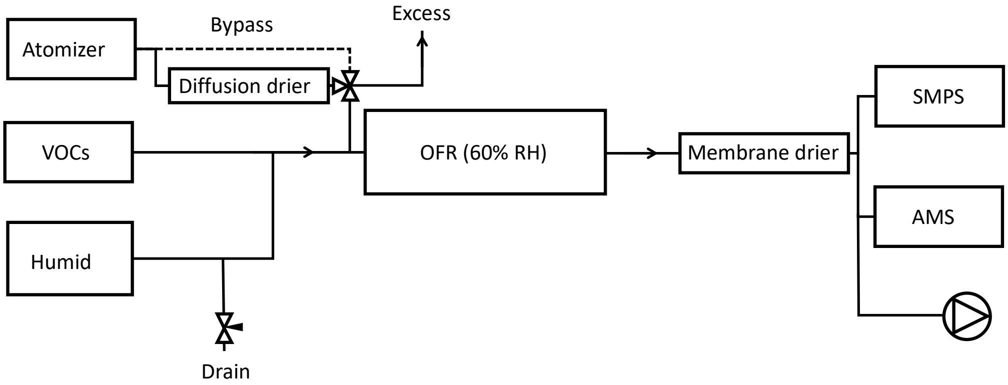


Figure 1. Experimental set-up. Seed particles were either dried or maintained in a liquid droplet. By changing the drain flow, the flow from the atomizer was varied without perturbing the VOC concentrations in the reactor. Total flow through the reactor was 5 lpm and RH was kept constant at 60 % by varying the RH of the humid flow.

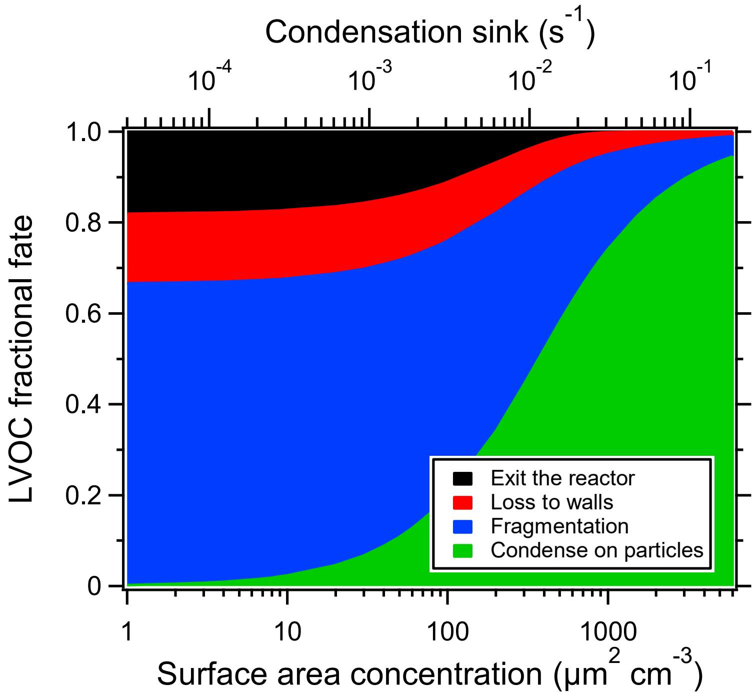


Figure 2. The fractional fate of LVOCs as a function of particle surface area concentration, using the model of Palm *et al.* (2016~~). A molecule is assumed to fragment after reacting with OH five times.~~), with the same OH reaction rate ~~was ~~(1 x 10^{-11} cm^3 molecs^{-1} s^{-1}~~.~~) and assuming fragmentation after reaction with OH five times. For reactor settings, see text.

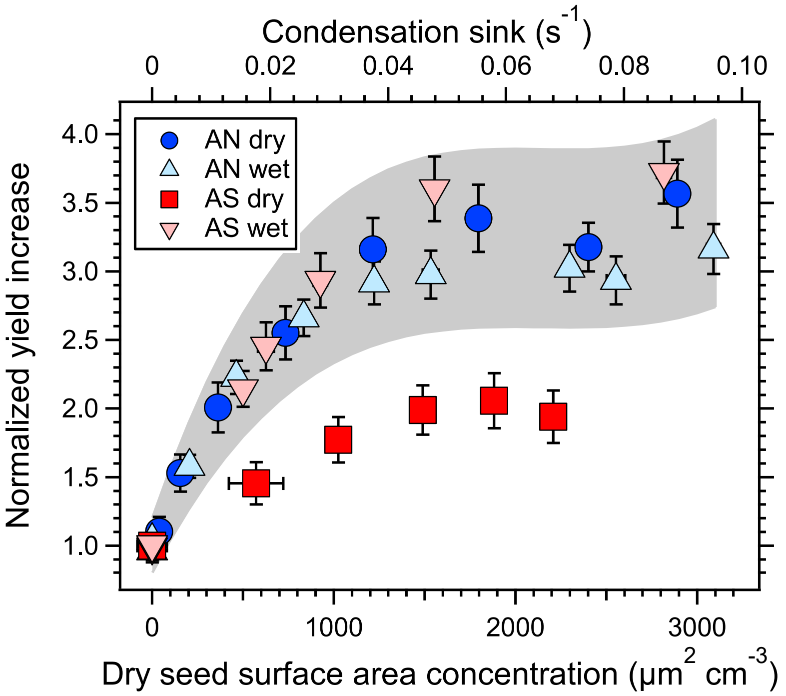
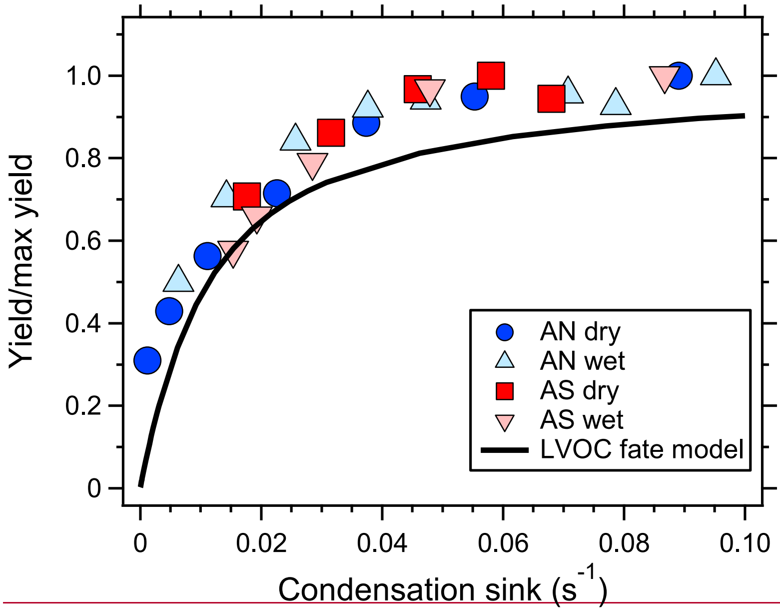


Figure 3. The increase in SOA yield from a mixture of m-xylene and α-pinene at different dry salt seed surface areas, normalized to the yield from experiments with no seed particles. The corresponding condensation sink is shown on the top axis. Error bars denote 1σ of the measurements. The grey area represents ±20 % of the three experiments where the seeds are not effloresced to illustrate the expected repeatability of the experiments and the fact that the dry ammonium sulphate results are the only ones falling outside of this range.



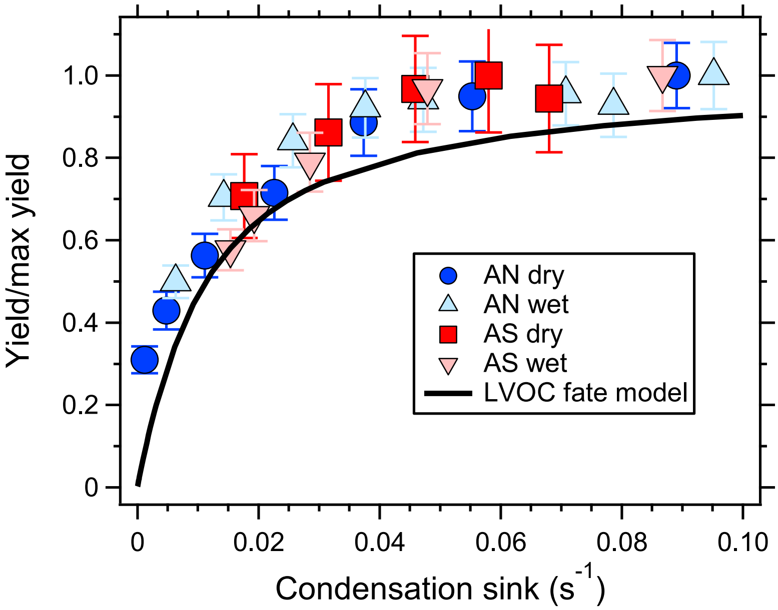


Figure 4. ~~The data~~SOA yield increase, from ~~Fig. 3~~a mixture of m-xylene and α-pinene, normalized by the maximum SOA yield increase and plotted against the dried seed particle condensation sink. Error bars denote the propagated uncertainties (1σ). The black line shows the fraction of condensed LVOCs according the model of Palm *et al.* (2016).

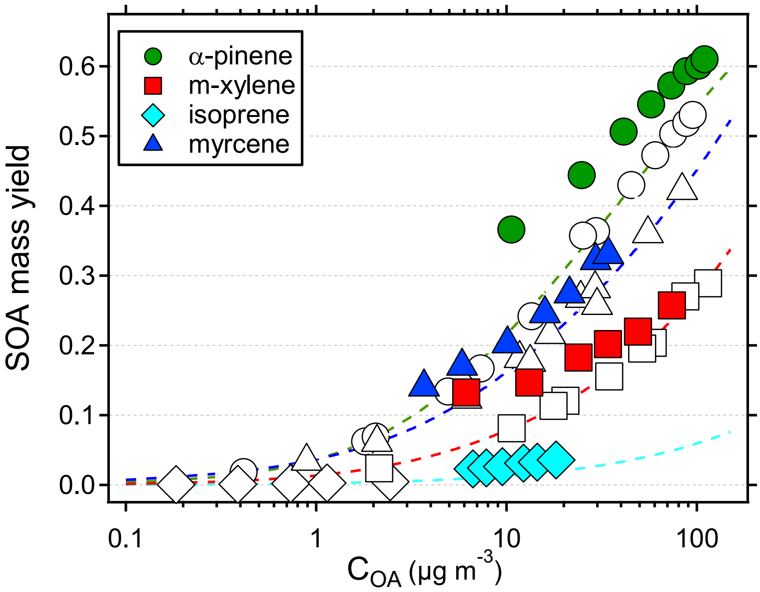


Figure 5. Recalculated SOA mass yields from Ahlberg *et al.* (2017) as a function of organic aerosol mass concentration (C_{OA}). Assuming an effective condensation sink of 1/3 of the reactor output, the inverse of the fraction condensed in the LVOC fate model from Palm *et al.* (2015) was multiplied with the measured yields. Coloured symbols are recalculated values, and original values are represented with the same symbol but no colour. Dashed lines show the VBS models constructed from the original data.

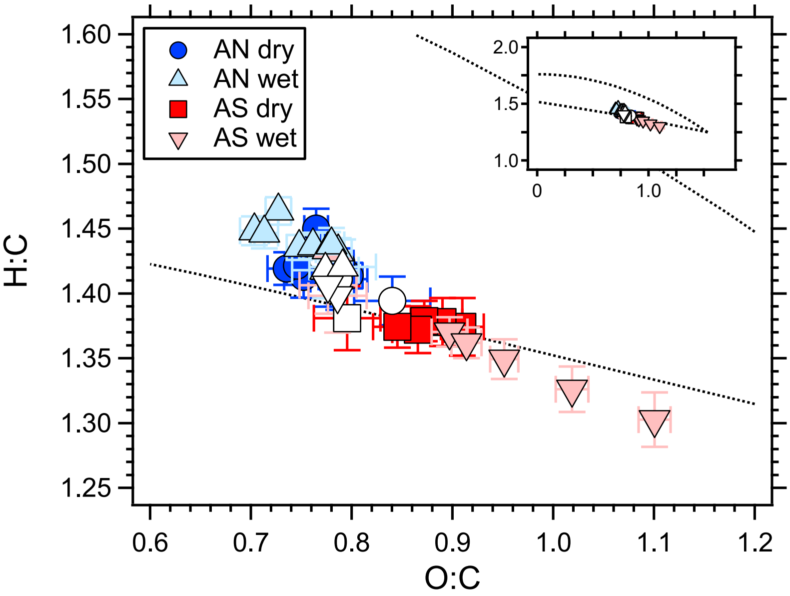


Figure 6.Van Krevelen diagram showing the ~~SOA~~ elemental ratios of ~~the~~SOA from a mixture of m-xylene and α-pinene, with different ~~experiments~~seed particles. The white markers represent SOA without seeds for corresponding symbol experiments. In general, O:C increased with increasing seed particle concentration. The dotted lines represent the Ng-triangle (Ng et al., 2011a) translated to the improved ambient elemental ratio parameterization (Canagaratna et al., 2015), to orientate the reader. The insert shows the same figure with different axis ranges, illustrating the fact that all data is within a relatively narrow range compared to e.g. ambient values.