

Interactive comment on “On the effects of hydrocarbon and sulphur-containing compounds on the CCN activation of combustion particles” by A. Petzold et al.

Anonymous Referee #4

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General comments:

The manuscript presents an assessment of the influence of sulfuric acid and organic coatings on the CCN activation of combustion particles. The analysis is based on a series of measurements (CCN, particle hygroscopic growth and volatility, particle size distribution and chemical composition) conducted during the PartEmis project. Many of these measurements have been previously described in a series of papers. In this manuscript the authors show a synthesis of this impressive data set to address two specific questions, namely the role of the organic fraction and the role of volatile

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condensation particles for CCN activation. These are interesting scientific questions and the attempt of synthesis and further interpretation of this large data set is definitely worthwhile. However, in the current form the manuscript has still some major problems that need to be addressed before publication.

One general problem I encountered reading the manuscript, is that the description of the data presented in the figures and tables is often not very precise. Several experiments were conducted at various conditions: Different fuel content (high, medium, low), different cruise conditions (modern, old), and for each of these conditions measurements were made at different sampling probe positions. Therefore it is necessary to specify exactly under which conditions the presented data were acquired. However, for most figures and tables this is only partially explained. While I will point only out specific instances, that especially detract from understanding the manuscript, I appeal to the authors to take special care that all the necessary information is provided for each figure and table in the manuscript. Some of the comments below may result from misunderstandings due to imprecise description of the data in figures and tables. In this case the misunderstandings should be easy to clarify.

Whenever error bars or uncertainty ranges are presented, it always needs to be specified, what those error bars represent (e.g., standard deviation of a mean, confidence intervals, measurement uncertainties, etc..).

Major comments:

- 1) Introduction: Since previous results on the PartEmis experiments have already been published, it would be good to qualitatively summarize the main results and the remaining open questions in the introduction.
- 2) Figure 3: For the modern cruise conditions the edge positions of the probe (cf. Figure 1, characterized by a lower T exit) seem to be missing in Figure 3. Please explain.

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3) Page 2608, line 24ff: The VTDMA and HTDMA measure the volatility and hygroscopic growth of the particles. In principle, volatile or soluble organic species could contribute to the volatility or water uptake. Therefore, the sulfuric acid content derived from such measurements is in principle only an 'equivalent' sulfuric acid content, representing all the chemical species contributing to volatility and water uptake. If there are good arguments why the authors expect sulfuric acid to be solely responsible for volatility and water uptake, then these should be stated. Otherwise the above distinction should be clearly explained in the paper.

4) Figure 10: This figure is not explained sufficiently, although it is crucial for the understanding of the following analysis. It is stated (on page 2611, line 15) that 'Figure 10 shows growth curves for particles of a dry size of 100nm'. Later in chapter 3.5 it is stated that 'the overall growth behavior of the combustion particles at the given experimental condition was determined from the entire data set as can be seen in Figure 10'. This leaves the following open questions:

(a) Are the data shown in Figure 10 an example of representative scans from each fuel content, or is this the entire data set, or do the data points maybe represent averages over all probe positions? In either case it is necessary to explain exactly what is shown here.

(b) The legend for the data points should show the respective fuel content and not a range of soluble volume fractions. The respective soluble volume fractions are the appropriate labels for the fit lines. However, this leads to another unclear point, that made it difficult for me to follow the analysis throughout the rest of the manuscript. What exactly is the meaning of the range of epsilon in the high and medium sulfur case? Certainly, in Figure 10 only one line is visible for each case. Does the range correspond to the uncertainty of the fit shown in Figure 10? In Figure 11 two data points are presented for the medium and high sulfur case, corresponding to epsilon of 0.8 and 1.2; 2.7 and 3. Do these illustrate the extreme cases of the ranges introduced in Figure 10, or does it mean that there are only two distinct values of epsilon derived

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in each case (maybe corresponding to different cruise conditions)? If the latter is the case, the use of a range is incorrect and misleading.

5) Figure 12: Why is the value of epsilon now 3.0 and not 2.8-3.0? The last sentence of the figure caption is confusing: What measurements precisely?

6) Figure 13: This figure illustrates that the particles sampled from the edge positions of the probe show diminished hygroscopic growth. The authors state that these particles also contain higher nonvolatile OC fractions and often show higher activation diameters (Table 3). Thus the authors conclude that high nonvolatile OC content increases the activation diameter. However, in this work, the hygroscopic growth factors are consistently used to derive the sulfuric acid content (Figure 8) or soluble volume fraction of the particles. Thus, looking at figure 13, my first interpretation would be, that the particles sampled from the edge positions simply contain less soluble material (sulfuric acid), and are therefore less efficient in water uptake and less efficient CCN (higher Dccn). Thus the observed correlation in Figure 14 could be a coincidence due to the anomalous sampling position. I think the authors need to at least address this possibility and provide convincing arguments against it. Only then I would be convinced that the decrease in water uptake and increase in Dccn is caused by the high nonvolatile OC fraction rather than missing soluble material.

7) Page 2616, line 1ff The derivation of the Dccn (ensemble) needs to be explained in more detail. Figure 11, bottom panel, does not show a Köhler curve (the Köhler curves are shown in the top panel). The line in the bottom panel shows the (theoretical) dependence of the activation diameter on coating volume fraction for an insoluble particle coated with sulfuric acid. Was this line used to calculate Dccn ensemble? For clarity, please also state the respective Dccn (ensemble) either in the text, in a table or in the figure legend of figure 14.

8) Figure 14: From the range of epsilon I assume these data represent medium sulfur fuel content, and should thus correspond to the data in Table 3. However, Table 3

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contains three (usable) data points with nonvol. OC/EC fractions in the range of 0.3–0.35. In Figure 14b I find only one data point in this range. If data points were omitted, this needs to be stated and justified. If the data in Figure 14 are different data than in Table 3, this need to be explained also. It seems to me that the data in Table 3 do not show such a clear correlation between nonvol. OC/TC and activation diameter as Figure 14b. Please explain.

Is the dependence of Dccn on nonvol. OC only found for medium sulfur content? If you do not show the rest of the cases, please state if the correlation is present or absent. If you observe the correlation only in the medium sulfur case, the statements in abstract and conclusions might have to be limited to some extent.

9) Table 5 This table needs to be explained more clearly: Is the activation diameter the 'measured' or the one derived from the ensemble value of epsilon? What does the uncertainty estimate mean? Please include the experimental conditions for each case (Fuel content etc.). Please give a more detailed explanation how the activation diameters for the nonvol. OC fraction of 0.5% were derived. If no OC fraction is mentioned, does this correspond to a nonvol. OC fraction of 0 (i.e., did you extrapolate the correlation of Figure 14 to lower values)? Or does the nonvol. OC fraction correspond to average conditions during the PartEmiss experiment? In the latter case, this nonvol. OC content should be specified as well.

Minor Comments:

- 1) Page 2612, line 1: Figure 11, top panel, $\tilde{\epsilon}$
- 2) Page 2615, line 3: Should this read 'Eq. 4' instead of 'Eq. 3'?
- 3) Table 3: What is the meaning of a range in probe positions (e.g. 9–7 etc $\tilde{\epsilon}$)? Was there only 1 measurement taken during those 3 sampling probe positions or were the measurements so similar, that they were combined to 1 data point afterwards?

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 2599, 2005.