

Interactive comment on “Behavior of CCN to CN fraction during aging and mixing processes of atmospheric particles” by S. Rojas et al.

Anonymous Referee #2

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The paper by Rojas et al. studies the relationship between cloud condensation nuclei (CCN) and total aerosol concentration (CN) for various air masses with different origins. Furthermore the authors have studied the influence of heating the aerosols sample through a thermo-desorber on this relationship. One of the main objectives was to study the influence of the aging process on the evolution of CN to CCN.

The authors claim that they have observed an active chemical layer on the surface of the particles “*containing more hygroscopic properties*” that has favoured the particle growth.

Specific Comments:

I have few major comments in regards to this observation.

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1. When one uses a thermo-desorber (thermodenuder) it is extremely important to properly characterise them. Where was the temperature of 220°C measured? Was the temperature measured in the air stream or was it the temperature of the walls of the oven? Even if you have measured the temperature of the air stream inside the oven it is still not the maximum temperature that your aerosols were exposed to. The maximum temperature depends on your flow rate. The main question is have you characterised your heater (oven) in laboratory experiments and proved that at the temperatures you report (measure) you have managed to volatilise components such as ammonium sulphate or bisulphate?

2. When using a thermo-desorbers one should be very cautious to properly measure the size of the aerosol prior and after heating in order to come to conclusions on whether part of the aerosol has volatilised or not. Measuring the size distribution of a polydisperse sample with an SMPS before and after heating could due to the noise present, at relatively low total particle concentrations below 1000 cm^{-3} , give misleading results. That is the reason that the thermo-desorbers are used within a TDMA where a monodisperse portion of the aerosol is volatilised. In the experiments presented within this paper authors come to the conclusion that: *“First, the comparison of both aerosol size distributions allows us to verify that the size of the particles is not altered by the thermo-desorbing experiment after they passed through the oven. It is clear from these measurements that there is no pronounced difference between these aerosol size distributions.”*

I have to fully disagree with this conclusion. A detailed analysis of the particle size distributions before and after heating (Figures 3e, 4e, 5e, and 6e) clearly shows a shrinkage of the particles due to heating. This is more pronounced in figures 5e and 6e than in 3e and 4e (although present in all of them). A rough estimate from figure 5e shows that i.e. particles of 300nm have evaporated to at least to 250nm, if not more. This corresponds to a reduction in the volume to $(205/300)^3 = 58\%$!!!! More than 30% of your volume has evaporated!! There are a number of other cases showing even larger parts of the

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volume being evaporated (particles smaller than 100nm in the clean marine case Fig 3e). The large fraction being evaporated is not an unexpected result. Especially for the marine aerosols there have been a number of publications showing that these particles are volatile at temperatures above the decomposition temperatures of sulphates.

Therefore you cannot claim that: *“This result well indicates that if an alteration occurs on the particle, only the particle surface seems affected. This observation confirms that the volatilization resulting from the thermo-desorbing does not affect the bulk composition but only the surface composition of the particle.”*

3. The authors claim that they have observed a larger change in the CCN/CN ratio due to heating on 4th and 1st of April, Figures 5 and 6 respectively, than in the other 2 cases. In regards to the previous comments your particles were much more modified due to heating (a larger volume has evaporated) on the 4th and 1st of April and this could explain a difference in the CCN/CN ratio. There is no proof that the portion you have volatalised was due to *“chemical transformation of the particle surface leading to the development of surface coating of inorganic species such as nitrate and sulfate, and finally to the formation of more hygroscopic particles.”* Sulphates are significantly present in both marine and anthropogenic aerosols.

4. My major comment would be: The authors claim that they have observed a difference in CCN/CN ratio before and after heating the samples. Careful observation of figures 5d and 6d and the error bars presented on them clearly show that the error bars overlap for all of the data points. The authors have to prove that the two cases (before/after heating) are statistically significant with 95% confidence. A simple t-test would show that. Looking at the error bars I am fairly confident that this cannot be proven and therefore puts into question one of the main conclusions of this paper.

Technical corrections

1. The y-axis on some of the size distribution data (figures e) is presented as $dN/d\log D_p$ but on others as dN . Should make all uniform and possible $dN/d\log D_p$

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2. Some figures have *Ref* and *Four* in the legend for non heated and heated samples respectively while some have *Ref* and *ThD*. Make all legends uniform.

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