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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Intercomparison of four different cascade impactors for fine and ultrafine particle sampling in two European locations" *by* A. S. Fonseca et al.

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We appreciate the detailed comments by Reviewer #2 and have now incorporated major changes and additions to the text which we believe have increased the robustness and clarity of our interpretations. This has been possible by also addressing the helpful comments of Reviewer #1. The manuscript has been revised in order to carry out the suggested amendments, and in our opinion the changes introduced after addressing both reviewer comments help with the clarification of the underlying causes for the differences in size distributions obtained, and in this way strengthen our interpretations.

General comments:

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- The authors have conducted size resolved aerosol sampling by four cascade impactors at two European sites and size distributions were compared by different type of impactors. The authors found that the best agreement regarding mass size distributions was obtained with the nano-BLPI, independently of the aerosol load and aerosol chemical composition by taking the BLPI as an internal reference. The authors also showed the size distribution of ionic components, and concentration of nitrate was considerable reducing in NanoMOUDI compare to BLPI and nano-BLPI for outdoor sample in winter campaign in Prague. The authors attribute this difference is due to dissociation of ammonium nitrate by internal rotating mechanism of NanoMOUDI which heat the impactor causing up. The reviewer think the topic of collection of ultrafine particle is important from the aspect of health effect issues of ultrafine particle, however I don't recommend publishing in ACP by following reasons. Although the authors speculate the cause of difference in size distribution obtained by different cascade impactors, the reviewer thought the evidence is too poor to accept the author's speculation. For example, the author describe that the rotating plate generates heat and that in turn rising temperature inside the NanoMOUDI. The reviewer wonder is it really? and if so, want to know how much temperature rise in this study. Further, the reviewer want to know how this increase temperature influence on size distributions and dissociation of ammonium nitrate in quantitatively, and to check the results of measurement. At least, the authors must show the temperature data inside NanoMOUDI.

Response: With regard to Reviewer #2's first comment on the temperature inside the NanoMoudi instrument, we verified our records and saw that unfortunately the internal temperature of the instrument during sampling was not recorded due to limited internal memory. However, our log books recorded that, for example, the instrument's temperature inside the cabinet increased from 18.8 °C at the beginning of sampling in Prague, (outdoor campaign) to 26.6 °C after 4 hours sampling, and then increased to 31.6°C at the end of one of the sampling periods As the Reviewer may observe, this temperature increase is significant and able to explain dissociation of ammonium nitrate which has been reported to take place with increasing temperature (Talbot et al. 2016; Allen et

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al. 1989; Stelson and Seinfeld 1982). The same is true of ammonium chloride (Pio and Harrison, 1987a,b; Allen et al., 1989). Quantitative estimation of nitrate loss is not possible, as it requires knowledge of a number of variables which is not available, i.e. partial pressures of nitric acid vapour, ammonia and water vapour within the impactor, and internal pressure at each stage. However, as noted, there is ample theoretical and practical evidence of destabilisation of NH4NO3 and NH4Cl as temperature increases in the cited literature. In addition to this, in order to reply to the Reviewer we have carried out additional tests in our campus with the same nano-Moudi unit which was used during the campaigns. We put one temperature sensor close to the filter substrates and another one outside the nano-Moudi cabinet. The results showed that temperature near the filter substrates was found 3.2-3.9 oC higher than those outside cabinet in the runs without filter rotating. In the runs with filter rotating, the temperature near the filter substrates showed an increase of 6.1-7.7 oC. Rotating mechanism makes the temperature inside the cabinet increase an average of 3.0 °C, suggesting that the heat inside nano-Moudi is also generated from other source (the electric current in the sensor board of nano-Moudi). With these recent experiments and based on our log books from the campaign we believe we are able to demonstrate that the internal temperature of the instrument did increase significantly and support our conclusions on nitrate dissociation. This is now reported in the text: “This effect would not be so prominent in outdoor air, given that the instrument does not reach such temperature increments since it was kept inside an air-conditioned cabin with a temperature continually lower than 20ËŽC while indoors, the temperature was continually higher than 23°C. For one sampling exercise outdoors, in Prague, the instrument’s temperature shown on nano-Moudi cabinet’s screen increased from 18.8 up to 26.6 °C after 4 hours sampling, and then increased up to 31.6 °C at the end of one of the sampling periods (3 days sampling; 72h). The temperature increase (both indoors and outdoors) was significant and able to explain dissociation of ammonium nitrate which increases progressively with increasing temperature (Talbot et al. 2016; Allen et al. 1989; Stelson and Seinfeld 1982). Ammonium chloride is known to behave similarly (Pio and Harrison, 1987a,b; Allen et

al., 1989)." With regard to the quantification of this dissociation process, we are unable to provide quantitative data due to the experimental nature of our campaign: if sampling had been carried out in a lab chamber with known ammonium nitrate concentrations we would have been able to quantify the losses. However, given that we sampled urban aerosol and had no prior information on the ambient concentrations of this species, we are unable to quantify the losses inside the impactors (the nano-Moudi and also the other impactors). Therefore, due to the experimental design we are unable to produce the quantitative estimates requested by the Reviewer.

- The second, the reviewer did not feel what is the implication of this study. What is recommendation way to collect ultrafine particle? Please clarify this.

Response: We agree with the reviewer that more emphasis should have been given to recommendations. These have been now extended and highlighted in the conclusions section:

"The conclusions from this work allow us to extract the following recommendations with regard to ultrafine particle sampling with cascade impactors: - To avoid particle bounce and increase the accuracy of the size cuts, impactor substrates should be greased especially in areas and seasons with low humidity. - Detailed assessments of the sampling duration should be carried out to allow sufficient collection of material on each stage for adequate quantification without overloading the upper collection stages. Common approaches to avoid particle overloading include using multiple-orifice collection stages, and rotating collection substrates (Marple et al. 2014; Marple et al. 1991). - Attention should be paid to volatilization issues during aerosol transport inside the impactors especially with regard to temperature increases associated with internal rotating mechanisms and the electric current in the sensor board of nano-Moudi. - Attention should also be paid to sample storage, to avoid evaporation of already deposited particles that may lead to a decrease of mass on a given stage. This evaporation would modify the observed aerosol size distribution, and would affect all impactor types."

Specific Comments:

1) Page 6, Lines 15 day L min-1 What means “L”? Please remove “L”.

Response: The authors apologize for this typo. The text was corrected as follows: “90 000 vehicles day-1.”

2) Page 7, Lines 12-13 PTFE filters PET foils are used in nanoBLPI as collection media. Some studies show the sampling media also influence of size distribution even if using the same impactor. Do you check the effect of sampling media on size distribution?

Response: The collection substrate is indeed an issue with impactors. The main issue affecting the size distribution is the thickness and the porosity of the collection substrates (see e.g. Fujitani et al., 2006). We did not check the influence of the sampling media on the size distributions, given that we used the substrates recommended by each of the manufacturers for each respective impactor. The comparison of the results from a single impactor with different impaction substrates is indeed an interesting study, but it was not the focus of ours. In the case of the nano-BLPI, we selected Mylar substrates given that they allowed us to quantify mass size distributions and also to characterize particle chemical composition (e.g., with ion chromatography). The validity of the size distributions obtained was verified by comparison with our internal reference (Berner impactor), which had been previously calibrated (with the method described by Hillamo and Kauppinen (1991) for the fine stages and by Štefancová et al. (2011) for coarse stages). Therefore, for this reason we did not intercompare filter substrates (this was not the purpose of our study), even if we agree with the Reviewer that it is an interesting topic for discussion.

3) Page 8, Lines 3-6 The NanoMoudi, in order to protect its electrical components, was kept inside an air-conditioned cabin with a temperature continually lower than 20°C and a metal pipe (about 300 cm long) was extended through the roof of the building. The air-condition cabin and metal pipe were only used for NanoMOUDI?

Response: These conditions were specific to the nano-Moudi in Prague, given that it is a more delicate instrument and it needed protection from the cold weather in winter. However, in Barcelona the Nano-Moudi was used under exactly the same conditions as the other impactors. This was also the case in Prague in the indoor experiments.

4) How these effect on size distribution? The reviewer expected higher temperature inside the cabin than outside, so it is easy to evaporate semivolatile materials in NanoMOUDI sample and there is a probability of particle deposition loss inside tubing.

Response: We agree with the reviewer that this could have been the explanation if we had only observed this pattern in the Prague outdoor samples (where the location of the Nano-Moudi was different to that of the other impactors). However, we observed the same type of size distributions from the nano-Moudi in all environments (Barcelona, Prague outdoor and Prague indoor). Therefore, we believe that the volatilization taking place inside the nano-Moudi was not explained by the temperature inside the cabin in Prague that was kept below 20°C but by the instrument's internal mechanism and design causing internal heating of nano-Moudi impactor (see above). Particle deposition losses inside vertical tubing would influence especially particles prone to diffusional transport i.e. particles bellow 100 nm. However, we observed just opposite behavior with maximum ultrafine particle mass recorded by nano-Moudi impactor.

5) Page 10, Lines9-10 All samples were equilibrated for a period of 24 hours before weighing in a temperature and relative humidity controlled room. Please add the average and sd for temperature and relative humidity.

Response: This information requested by the Reviewer was included in the text: "All samples were equilibrated for a period of 24 hours before weighing in a temperature and relative humidity controlled room (20.0 $\pm$ 0.2 °C; 45.4 $\pm$0.6 % RH)."

6) Table 2 Mean PM14* What mean for *?

Response: This was a mistake. The "*" was deleted.

7) Page 12, Lines13 M is Please change to Mi.

Response: This was corrected.

8) Page 13, Lines13 the instrument does not reach such high temperatures Please make clear how much temperature increase.

Response: Please see our reply to the first comment. The high temperatures reached by the instrument are now described in the text based on experimental data.

9) Page 13, Lines15-16 However, it is important to take into account that some differences in the results could be partially attributed to the differences in the real cut points for the selected size fractions. To prevent such problem, it is better to fit the certain size distribution such as lognormal size distribution.

Response: This comment refers to a section which was removed from the manuscript based on a comment from Reviewer #1.

10) Page 16, Lines9-11 The higher pressure drop in the stationary impactors (e.g., BLPI) may increase the probability of volatilisation of semi-volatile species during prolonged sampling, Please assess how this pressure drop induces evaporation of semi-volatile species in quantitatively.

Response: Please see our reply to the first comment. We are unable to quantify the losses inside the impactors given that our study was carried out measuring outdoor aerosol for which the initial concentration was unknown. The data requested by the reviewer may only be provided in an experimental chamber study, according to the authors. Nevertheless, if a particle was in equilibrium in the atmosphere than this equilibrium is disrupted by pressure drop as partial vapor pressure of a species decreases linearly with total pressure drop. This increases driving force for evaporation as it is equal to the difference between the equilibrium vapor pressure of the given species and its partial vapor pressure in the gas phase. However the situation is more complicated while a particle is incorporated into a deposit of particles where other processes

like diffusion in semiliquid mixture of other organics or Raoult's law play their roles. This process anyhow influences the measured concentrations and therefore our comparison. The information was incorporated into the corrected text: "However, drying of particles before they are deposited on a substrate may happen also in the BLPI and nano-BLPI due to higher pressure drops (at equivalent sizes) despite lower residence time in comparison with the nano-Moudi. This would increase the driving force for evaporation at those stages as it is equal to the difference between the equilibrium vapor pressure of the given species and its partial vapor pressure in the gas phase. However the situation is more complicated while a particle is incorporated into a deposit of particles where other processes like diffusion in semiliquid mixture of other organics or Raoult's law play their roles. This process influences the measured concentrations and therefore the impactors comparison."

11) Page 18, Lines20-23 Also, the residence time of particles inside the nano-Moudi low pressure stages is longer due to the lower volumetric flow rate in this instrument. All of this could thus explain the mass size distributions from the nano-Moudi being skewed towards smaller particle fractions during the Barcelona and Prague campaigns (Figure 4). Please (rough) estimate how this difference of residence time effect on size distribution.

Response: This statement was deleted from the manuscript since we have added the following text: "However, drying of particles before they are deposited on a substrate may happen also in the BLPI and nano-BLPI due to higher pressure drops (at equivalent sizes) despite lower residence times in comparison with the nano-Moudi. This would increase the driving force for evaporation at those stages, which would encourage particle shrinkage."

The lower residence time in BLPI and nano-BLPI decrease evaporation and therefore shift size distribution to larger particles in comparison with nano-Moudi. However, due to many complex processes (influence of pressure drop, temperature, particle composition, RH etc.) influencing the actual particle evaporation rate it is difficult to quantify it

for real aerosol and real impactors.

Further explanations regarding the influence of relative humidity were included based on a comment from Reviewer #1: “Although it is known that RH is lowered at each stage of any cascade impactor this decrease is only moderate for the first stages. For example, the pressure below stage 6 of the BLPI which corresponds to particles as small as 440 nm is only 6% lower than ambient. A similar value is found for nano-BLPI for equivalent stage. The nano-Moudi has even smaller pressure drops at equivalent stages. The drying becomes important for lower stages, however, it is known that kinetic effect limiting drying of particles would be more pronounced at lower temperatures in winter due to lower equilibrium water vapor pressure. In any case, atmospheric particles in the size range below 250 nm are comprised mostly of organics, especially in winter (see e.g Kubelová et al, 2015). These fractions of organics are often of semiliquid nature and this fact efficiently prevents bounce.”

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/acp-2015-1016/acp-2015-1016-AC2-supplement.pdf

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