

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 reviewer's comments and we agree that the data collected would have relevant implications for atmospheric science but major revisions are required. To make up for this, the manuscript has been revised in order to carry out the suggested comments and to improve its clarity. Modifications in the text are highlighted with track-changes (supplement document attached). We believe that the improvements based on the Reviewer's suggestions have increased the quality of the manuscript significantly and hope that it now may be up to the standards to the journal.

Comments:

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1) The authors mention that the greater RH environment of the summer in Prague would reduce the amount of particle bounce (Page 17 line 9-12) and potentially explain the results shown in Figure 1. However, at each stage in the cascade impactors, the pressure is reduced. This reduction in total pressure will also reduce the RH according to $RH_i = RH_{amb} \cdot P_i / P_{amb}$. Therefore, at each stage of impaction, the relevant RH to compare is the RH directly above the impaction stage according to the upper stage pressure. This number will be greatly reduced for the lower stages of impaction, regardless of the initial ambient RH. Therefore, particle bounce of ultrafine particles will be an issue for any cascade impactor.

Response: We agree with the reviewer that possible impactor artifacts have to be properly taken into account. We would like to stress that in the manuscript we are referring to the conditions during winter in Prague (outdoors). Here we would like to provide a number of arguments showing supporting our statement that particle bounce had a negligible effect in the Prague outdoor campaign:

First, it was winter season in Prague when higher RH was recorded. This is important as only few coarse particles were present and at the same time the high share of primary, less oxygenated organics was found (Vodicka, 2013, Kubelova 2015).

Second, the reviewer is right that RH is lowered at each stage of any cascade impactor. However, this decrease is only moderate for the first stages. To say it more precisely, the pressure below stage 6 of the BLPI, i.e. for particles smaller than 440 nm is by only 6% lower than ambient. Similar value is found for n-BLPI for equivalent stage. The situation is even better in Moudi as it has smaller pressure drops at equivalent stages.

Third, the particles once they are droplets need to experience relative humidity 40% or lower to dry due to hysteresis effects. It means that at least one stage lower they are still droplets. This is experienced by impactor users seeing droplets even on the fifth stage in case of BLPI (i.e. for 250 nm particles).

At lower BLPI stages particles can dry although we can discuss if drying is fast enough

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to influence deposition on the 4th stage in BLPI due to kinetic effect and short time of flight between the nozzle and the impaction plate. This kinetic effect will be more pronounced at lower temperatures due to lower equilibrium vapor pressure. Nevertheless, particles in this size range below 250 nm start to be formed mostly by organics, especially in winter (see many AMS publications with size distribution recorded e.g Kubelova et al 2015 for Prague). These organics are often of semiliquid nature and this fact efficiently prevents bounce.

Finally, we (and also others) made tests (unpublished data) that showed for BLPI that in winter with high RH there was no difference between two identical impactors when one of them used greased foils and the other one ungreased foils. The situation was different in summer at low RH. If ultrafine particles were "hard-ball like", e.g. when dry pure inorganic salts are used for testing, then the situation would have been different. However, for an ambient aerosol with high fraction of organics which is typical for Prague in winter the influence of bounce would be substantially reduced. All these aforementioned facts were added to the body of the manuscript.

2) The authors state they use a thin layer of grease (page 7 line 27 – 31) on the internal standard (BLPI). This should be stated in the abstract and conclusion. However on page 11 line 19-20, while discussing the sampling at Barcelona using BLPI (the internal standard), the authors state that the foils were not coated with grease. Which is it? I would not trust an impactor that was not coated with grease to be used as an internal standard. This would explain the agreement in PM0.25 – PM2 observed in Figure 2 and Figure 3 for the Barcelona samples. But it would also negate the fact that you had an internal standard, as the Barcelona sampling with BLPI would be prone to particle bounce artifacts.

Response: We apologize for the confusion created: the internal standard (BLPI) foils were always greased, in all locations and during all samplings. This sentence is confusing because it refers to the nano-BLPI, nano-Moudi and PCIS (not the internal standard), which were not greased in any sampling or location. We have now corrected the

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sentence as follows: "Also, a distortion of the size distribution due to bounce-off should not be neglected for Barcelona in the nano-BLPI, nano-Moudi and PCIS given that foils were not greased prior to sampling. The same artifact is not expected to occur during winter in Prague (outdoors). This is supported by previous tests from BLPI (authors' unpublished data) showing no difference between two identical impactors when one of them used greased foils and the other one ungreased foils." This issue was pointed out and is now highlighted in the Conclusions section as follows: "All the cascade impactors were loaded with uncoated substrates excepting for the case of BLPI which foils were coated." However, we agree that was missing in the abstract. To make up for this, we added the following sentence: "Only the BLPI substrates were coated with a thin layer of vacuum grease, therefore particle bounce that may occur during dry collection should only be considered for the other impactors."

3) I do not understand Figure 3. Why do the authors lump the mass concentrations into categories that do not match with the impaction cut-points? There is no cut-point at 250 nm for the nano-MOUDI and there is no cut-point at 1.0 μm for the BLPI. So how did the authors arrive at mass concentrations for PM0.25 and PM1 for these two cascade impactors? This should be stated directly in the manuscript. The authors state on page 15 lines 7 -9, that differences in Figure 3 can be attributed to difference in cut-points. This figure is then misleading to the readers and of no use as an intercomparison. As it is not a difference in collection efficiency or potential collection artifacts, but how the instruments are designed to operate.

Response: Figure 3 was now removed from the manuscript given that the grouping of the size fractions was not rigorous enough. Our aim with this was to compare the performance of the impactors for commonly used size fractions, but it was clearly not a good idea. Therefore we have now removed it from the manuscript and focus only on the actual size distributions. The text has been modified accordingly.

4) Figure 4. In order to assess the ability of the impactors to accurately assess the collection of ultra-fine and fine particles, one needs to know what the actual mass con-

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centrations of these particles are. It would certainly benefit the study to have some form of external validation that did not rely on a cascade impactor, such as filter sampling, or SMPS (or DMPS) to provide some external validation points for Figure 4. In addition, the authors suggest that this sampling for Barcelona was for 4 weeks (Page 17 lines 25) while Table 1 does not seem to agree.

Response: It would indeed have been very useful to have an additional external reference, but this was not possible for either of the locations (Barcelona and Prague). In addition, the external reference would have had to be the same for both locations, which complicated things even further. Therefore, we used the BLPI as external reference, given that we were comparing the same sampling technique (impaction) and with exactly the same instrumentation during all samplings. The only comparison we included is with the mean PM1 and PM10 size cuts concentration (with a Grimm laser spectrometer corrected with high volume sampler) in Barcelona for the same sampling period, in order to estimate the correlations of the concentrations measured. The original paragraph allusive to this is the following (Page 13): "The average PM14 mass concentrations and corresponding standard deviation obtained using the internal reference (BLPI) in Prague outdoors were $34.6 \pm 15.8 \mu\text{g m}^{-3}$. In Barcelona, the PM14 mass concentrations and standard deviation in summer were $15.2 \pm 2.1 \mu\text{g m}^{-3}$. Comparison of independent data from a Grimm laser spectrometer (corrected with a high volume sampler) and the impactors with PM1 and PM10 size cuts, was carried out for the outdoor campaign in Barcelona (4 samples). A slope of 0.98 and a R² of 0.7 was obtained for the PM14 for BLPI with PM10 from an online laser spectrometer (corrected with regard to reference instrumentation) whereas for PM1, a slope of 0.7 and a better fit of the data was obtained (R²=0.9). Similarly to BLPI, the nano-BLPI shows a slope of 0.7 and a R² >0.99 for the cut point PM1. The mass differences detected for PM1 suggest that impactors sampling artefacts such as particle blow off, particle wall losses and/or particle bounce occurred."

In addition, to provide an idea of the order of magnitude of particle mass concentra-

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tions, we included the comparison between the mean outdoor PM14 mass concentration (with BLPI) in Prague and Barcelona with previous results from 2008 winter campaign in Prague and from a 2014 summer campaign in the monitoring station at Barcelona (PM10=19.6 $\mu\text{g m}^{-3}$). This is the best we could do given the lack of concurrent reference monitoring of PM mass concentrations. This paragraph is included in page 11/12: "In Prague, the mean PM14 mass concentration measured outdoors (with BLPI) was $34.6 \pm 15.8 \mu\text{g m}^{-3}$ whilst in Barcelona (with BLPI) it was $15.2 \pm 2.1 \mu\text{g m}^{-3}$ (Table 2), in a similar order of magnitude than during previous results from 2008 winter campaign in ICPF (Schwarz et al. 2012; PM14=34 $\mu\text{g m}^{-3}$), and during a 2014 summer campaign in the monitoring station at IDAEA-CSIC (PM10=19.6 $\mu\text{g m}^{-3}$)."

As for the Reviewer's comment regarding the sampling duration in Barcelona, we agree that it was confusing. The text has now been modified as follows: "Outdoor sampling in Barcelona consisted of 4-day (during week-days) samples, each of them accounting for 96h (4 consecutive days). A total of 4 samples (4-days each) was collected."

This is in agreement with Table 1.

We agree with the reviewer that saying "Although differences were smaller, the same is true for the Barcelona summer campaign (4-week sampling, Figure 3)", can mislead the reader. We apologize for this. We have clarified this issue as follows: "Although differences were smaller, the same is true for the Barcelona summer campaign (4 samples in total, Figure 3)".

5) The use of IC to determine the mass of ion concentrations on each stage seems like a great idea. However, the authors provide very weak conclusions from these studies. Page 21 lines 3-5, the authors provide all ranges of explanations, so what is the use of the IC study? Again, it would be useful to know what the actual mass concentrations of the ions are in order to determine any artifacts from impaction sampling.

Response: We agree with the reviewer that IC data is a very useful tool for this work, and this is why we included it. The IC results aimed to support our interpretations of the

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mass data. The artefacts discussed in the paper (bounce, etc.) were discussed based on IC results on page 20, lines 15-18: "In outdoor air there is a clear decrease of NO₃-concentrations measured with the nano-Moudi, confirming the interpretations provided in the previous sections. The same is valid for fine chlorides that are missing on same nano-Moudi samples showing ammonium chloride evaporation (NH₄Cl)." This was one of the purposes. Secondly, using IC provides a possibility to identify contamination and bounce with regard to bounce of coarse particles. Nitrate evaporation is clearly seen on Moudi ambient samples from Prague in winter. The same is valid for fine chlorides that are missing on the same Moudi samples showing ammonium chloride evaporation. Therefore, using IC very clearly confirmed the evaporation artifact on Moudi samples. Even if this were the only benefit of IC analysis, we believe its use was fully justified. However, there is also another reason that justifies the IC analysis. The sensitivity of mass determination is actually worse than sensitivity of analytical determination of main ions. Therefore, if both independent methods lead to the similar results, the overall conclusions can be trusted more than those from one method only. An example of IC blank uncertainty recalculated per 1m³ of air for BLPI for 72 h sampling is below:

in $\mu\text{g m}^{-3}$: Cl⁻ = 0.0003 SO₄²⁻ = 0.00094 NO₃⁻ = 0.00134 Na⁺ = 0.0002 NH₄⁺ = 0.0002 K⁺ = 0.0002 Mg²⁺ = 0.0001 Ca²⁺ = 0.0003

Regarding the actual mass concentrations of the ions, we have modified the text to include mean mass concentrations for the ions mentioned in the text, and have added a Table in Supporting Information with the mean values for all of the ions (anions + cations) analyzed for each of the environments (indoor and outdoor) in Prague. The uncertainty of the blanks is also included in the Table.

6) If the temperature of the nano-MOUDI does indeed increase and effect volatilization of nitrate as the authors suggest, why is this not observed in the indoor samples? There is not a clear decrease in the nitrate signal in the indoor samples, as the authors suggest on page 20 line 18. In addition, there are no error bars on these data points, making any scientific interpretation difficult. There is also a decrease in the sulfate

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signal in the indoor samples, which is not expected to volatilize, suggesting an overall decrease in collection efficiency perhaps and not an effect of increased temperature.

Response: The text is now improved thanks to this suggestion, as the decrease in nitrate indoors with the nano-Moudi is indeed not very visible (in the text we used to refer to it as "less pronounced"). This can be explained as follows: it is well known that ammonium nitrate indoors dissociates to gaseous nitric acid and ammonia, not only due to higher temperature indoors but also due to dissociation equilibrium of ammonium nitrate being shifted to gas phase by chemisorption of released nitric acid to many surfaces especially walls. Therefore, nitrates present indoors are influenced by other forms of nitrate different to ammonium salts (e.g. sodium or potassium nitrate) that are not prone to dissociation. For this reason, the difference between Moudi and the other impactors indoors is much smaller compared to outdoors. This has been clarified in the text: "Nitrates present indoors are influenced by other species different to ammonium salts (e.g. sodium or potassium nitrate) that are not prone to dissociation. For this reason, the difference between nano-Moudi and the other impactors indoors (Figure 6) was much smaller compared to outdoors (Figure 5)"

With regard to sulphate, the lower concentration of both mass and sulphates on Moudi indoors are clearly caused by other factors. In this case, we believe an influence of bounce cannot be neglected as average RH indoors in winter was 23% RH. This is now discussed in the text: "The lower sulphate and mass concentration on nano-Moudi indoor samples were caused by other factors (possibly bounce) given that average RH indoors in winter was low (23%)."

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2015-1016/acp-2015-1016-AC1-supplement.pdf>