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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Applicability of condensation particle counters to measureatmospheric clusters" *by* M. Sipilä et al.

M. Sipilä et al.

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In responce to referee comments:

Referee 1:

The author team has provided an interesting paper on the experimental detection of sub-3nm atmospheric particles and/or clusters. Their analysis is based on two measurement techniques (PH-CPC and E-CPC), which were characterized in the laboratory, and then deployed in the field. While these techniques themselves are not new, their combination and careful characterization proved to be useful in approaching one of the frontal lines of current knowledge in atmospheric science, the origin of natural nano-particles. The salient result is that neutral molecular clusters seem to exist in the atmosphere at most times - at least in the lower atmosphere over the boreal forest;

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these clusters can eventually evolve into particle formation bursts. Although the origin and composition of these clusters continue to remain unknown, this paper is the first to suggest their existence by multiple measurements. I therefore recommend to publish this paper in ACP with minor revisions outlined below.

Improvements can be made by supplying more concrete numbers when illustrating measurements and comparing instrumental performance (see details below). More concrete recommendations are also given below.

-We will improve the manuscript by expressing the numbers when possible.

Since this paper is expected to be cited many times, special care is also advised with respect to the writing. While the language level is satisfactory in general, there plenty of unnecessary and re-occurring flaws which distract from the reading. Most notably, the definite and the indefinite articles are missing on plenty of occasions. I therefore appeal to the native speaking authors to make this also a literally "appealing" article. Otherwise, additional proofreading might be required.

-We will perform further proof-reading and correct the language.

Abstract:

"Both instruments showed similar concentrations": Quantify the deviation. The same also in the conclusions section.

-Concentrations were typically within the factor of 5 the same. This will be quantified in the revised manuscript.

Section 1, Introduction:

This section could be improved by adding one or two sentences at the beginning stating the general relevance of aerosol particles in the atmosphere.

-We will improve that point.

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p. 4375, l. 5, "some investigations": Write concretely what kind of investigations - laboratory, field, theory? This is hard to grasp for a non-specialized reader.

-Here we refer to the field measurements by Kulmala et al. (2005). That will be corrected.

l. 14, "are challenging": Why are such measurements challenging? Outline the most important physical constraints and technical drawbacks for a reader not familiar with aerosol science.

-There are several points making the detection of sub-3 nm particles complicated. First, because small clusters are extremely diffusive, the transport efficiency from the atmosphere to the instrument's detection system decreases rapidly with the decreasing particle size. Second, the interaction of small neutral clusters with the surroundings is very weak. Charging of them is not very efficient, and low concentration of clusters charged in an aerosol charger sets big demands on any electrical detection system. Condensation based techniques, however, can allow one to activate and detect neutral clusters below 2 nm in diameter (Winkler et al., 2008). Commercial particle counter systems are designed to have a zero background (no false counts) and therefore the lowest measureable particle sizes are around 3nm. By increasing the supersaturation of the working fluid this limit can be pushed towards smaller sizes. Problem is that at some point homogeneous nucleation is induced. Since an ordinary laminar flow CPC only counts the droplets, one can not distinguish between homogeneous and heterogeneous nucleation inside the instrument. Therefore the supersaturation should be in a safe regime, i.e. no homogeneous nucleation can occur. Techniques presented in our paper allow one to distinguish between homogeneous and heterogeneous nucleation and thus higher supersaturations can be used.

-We will improve that point in the revised manuscript.

Section 2: Structural deficits: The first text block has no section numbering nor header, but should be called "2.1. General approach" or similar.

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-We will improve that.

Section 2.1: Same as above: The first text block is very long but has, again, no section numbering nor header. (Should be "2.2.1. ...").

-We will improve that.

Section 3: General comment: In the laboratory, the authors studied solid and insoluble particles (Figure 1). The CPC battery paper of Kulmala et al. (2007) shows that the detectability of the smallest particles in a CPC may be pending on the affinity of their chemical composition to the CPC working vapor. In the atmosphere it seems that the smallest particles tend to be hydrophilic. Could you comment on how this effect may degrade the comparability of your laboratory and field PH spectra?

-Artificial WOx-particles used in the laboratory experiments are of course atmospherically irrelevant and the results from the laboratory experiment and the field measurements are not directly comparable. More over WOx particles were charged whereas the atmospheric sub-3 nm clusters were found to be mostly neutral. Data shown in figure 1 as well as in figure 2 are meant mainly for showing to the reader that the PH-CPC can detect those laboratory generated sub 3nm particles - or clusters. We would assume that chemical composition of the atmospheric clusters can have some impact on the activation probability and the detection efficiency of the clusters in both instruments. However, since the E-CPC data matched reasonably well to the PH-CPC data independent on the E-CPC working fluid, it is clear that the effect of cluster chemical composition on the detection probability can not be very high.

p. 4381, l. 15, "challenging tasks": Again, state briefly what the most important limitations of the existing measurement apparatus are. The same also in the abstract, p. 4374, l. 12.

-There is no reference instrument available for sub-3 nm neutral particles. Therefore there is no option to determine e.g. the concentration of sub-3 nm calibration aerosol

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particles.

p. 4381, l. 15, "ions were filtered away": State briefly how this was done.

-Ions were filtered using a co-axial electric filter described on p. 4379 l. 17-21

p. 4382, l. 5, "Gaussian" ! "Gaussian-shaped"

-We agree.

p. 4382, l. 7. This sentence can be dropped.

-We agree.

p. 4382, l. 17, "water" - which degree of purity?

-Water we used was deionized Milli-Q water.

p. 4385, l. 14, "was measured ... from time to time". How often did you perform these checks concretely?

-These checks associate to diffusion battery measurements, which were performed usually 3 times a day.

Section 4:

p. 4389, l. 3: Can you comment on the expected probability of survival (in orders of magnitude) for thermodynamically unstable clusters between the inlet and the point of activation?

-It certainly depends strongly on the cluster composition. For the reasonably high vapour pressure compounds the survival probability would be practically zero. But for extremely low vapour pressure compounds the cluster decomposition rate can be low thus increasing the probability of survival. But we cannot quantify that.

p. 4390, l.25, "organic chemistry" is a very broad term. Which is the particular role the authors think organics could play?

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-For example sesquiterpene oxidation products could in theory induce nucleation of those clusters (Kurtén et al., 2007). At this point we, however, would want to avoid too much speculation. Much more detailed analysis and comparisons to the precursor concentrations, meteorological parameters, etc. are needed before we can say more on the origin of these clusters. We will try to clarify that point in the text.

Section 5: Last sentence of the section, "without doubt". It is difficult to understand what you mean by this statement. Reformulate.

-We mean that these measurements strongly support the activation type nucleation as new particle formation mechanism. We'll rewrite the last sentence.

Figures: Figure 2: "ambient indoor"? Do you mean "indoor air", i.e. "room air"?

-Yes, we mean indoor air.

Figure 4: The subfigures should be labeled (a) and (b) and referred to in the text the same way.

-We will correct that.

Figure 5: Make a brief comment how the concentration minimum between 08:00 and 10:00 comes about, possibly on the basis of meteorological measurements. Is this horizontal advection or vertical mixing? Also, indicate by vertical bars the events of the four measurements shown in Figure 6.

-Concentration minimum is due to boundary mixing after the sunrise. We will modify the figure following the referee suggestion.

Figures 6 and 10: What is the presumed reason for the dip in the data around MCA channel 630?

-We suspect that it is a technical problem in the CPC's photodetector. That is mentioned in the caption of Fig. 10.

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Language/Style This is just an incomplete list I made. The 1st sentence in the abstract could be improved. "during 1 March to..." ! "between 1 March and..." "were from ca. 1000 to" ! "ranged between ca. 1000 and" "Somewhat" is a quite redundant word in a scientific paper. Try to support the arguments by concrete numbers. "to get an idea" - too informal. "pulse height", "pulse-height", or "Pulse-Height"? "PH spectrum" of "PH-spectrum"? "vast amount of ions" - maybe better a vast "number of ions"? p. 4389, l. 2, "extend" ! "extent" p. 4389, l. 4, "should be rather poor" ! "is expected to be rather poor" "from few tens to few hundreds", "up to few tens": missing articles The definite and the indefinite articles are missing on plenty of occasions.

-We'll correct the language and do further proofreading for the final manuscript.

-We wish to thank the referee for useful comments.

References

Kulmala M., Lehtinen K. E. J., Laakso, L., Mordas, G., Hämeri, K.: On the existence of neutral atmospheric clusters, Boreal Environ. Res., 10, 79-87, 2005.

Kurtén, T., Bonn, B., Vehkamäki, H., and Kulmala, M.: Computational study of the reaction between biogenic stabilized Criegee intermediates and sulfuric acid, J. Phys. Chem. A, 111, 3394-3401, 2007.

Winkler, P. M., Steiner, G., Vrtala, A., Vehkamäki, H., Noppel, M., Lehtinen, K. E. J., Reischl, G. P., Wagner, P. E., and Kulmala, M.: Heterogeneous nucleation experiments bridgin scale from molecular ion clusters to nanoparticles, Science, 319, 1374-1377, 2008.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 4373, 2008.