Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2019-23-AC1, 2019

Atmospheric Measurement Techniques Discussions

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Interactive comment on "Humidity effects on the detection of soluble and insoluble nanoparticles in butanol operated condensation particle counters" *by* Christian Tauber et al.

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Received and published: 27 March 2019

We appreciate the thoughtful comments by referee 1. For discussion purposes we would like to respond to the general points raised.

There are some interesting results but the presentation could use some work. Primarily, the humidity effect for detection of NaCl nanoparticles is prominently displayed in a couple of figures but this effect is nearly lost because of all the text about charge or charging effects. The authors need to motivate, and consider significantly paring down the data and discussion of charge effects.

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Discussion paper

Also important is that there is a lack of discussion on how others could apply the humidity effect for these types of particles.

We acknowledge the well-justified comment on how others could apply the humidity effect for these types of particles. Generally, we think that particle counting at the detection limit of ultra-fine condensation particle counters has to be treated with care. Due to high particle number concentrations in the nucleation mode, atmospheric measurements of soluble and insoluble nanoparticles might lead to wrong data interpretation. The lowest detectable particle size, i.e. the cut-off diameter of a CPC, is among the largest sources of inaccuracy in the sub-10 nm particle concentration measurement (Kangasluoma et al., 2018). Given that not only seeds of different chemical compositions but also solubilities are present in the atmosphere – these uncertainties on the number concentration need to be considered. A straightforward approach to assess the uncertainty of a humid sample flow is to dry the inlet flow of a CPC by e.g. using a Silica gel dryer or Nafion dryer which is a common method during ambient measurements. Additionally, the inlet RH should be monitored and kept below a threshold value in order to narrow down the uncertainty from the humidity dependent change of the cut-off curve in the case of a soluble seed.

Hygroscopicity measurements of particles in the targeted size range further improve the assessment on the uncertainty of the number concentration. The location of the measurement site is also a clear indicator of a possible enhanced contribution of hygroscopic seed particles, i.e. when the measurement site is located by the coastline. Thereby the accuracy of the data interpretation would increase. Even without these additional measurements, the location of the measurement site can be used for data interpretation. As a result, studies that consider sea spray as a particle source should consider the effect of humidity on the particle detection efficiency. Furthermore, the enhanced activation of soluble particles can also be used to improve the detection efficiency for hygroscopic seeds.

A concerning factor as to whether these results apply to the atmosphere: Are

there actually any nanometer-sized NaCl aerosol in the atmosphere?

The important fact, which will be more highlighted in the updated manuscript, is that in our case NaCl served as a representative hygroscopic seed particle. It was selected for our studies, since it is known to be very hygroscopic and well characterized by different studies like Biskos et al. (2006) and Krämer et al. (2000). Clarke et al. (2003) were able to characterize the size distribution of particles in the atmosphere produced by breaking waves. They could demonstrate that those particles cover the size range from 10 nm to greater than 10 μm. Regarding the chemical composition of nanoparticles in marine surroundings, M. J. Lawler et al. (2014) conducted TDCIMS measurements in Mace Head, Ireland. The composition measurement of particle between 15-85 nm showed measurable levels of sodium and chloride. Sea spray is a complex mixture of inorganic salts and organic material and a recent study by Zieger et al. (2017) showed that the hygroscopicity of the inorganic component is about 8-15% lower than of pure sodium chloride.

The discussion of the rearrangement / change in shape of these particles is missing any experimental description. This experimental data is a (another?) humidity effect and seems to be pertinent to the topic here.

At relative humidity below the deliquescence threshold NaCl particles with an initial mobility diameter between 19-200 nm undergo a microstructural rearrangement as shown by Krämer et al. (2000). Subsequently, G. Biskos et al. (2006) investigated the deliquescence and efflorescence of NaCl seeds with a mobility diameter between 6-60 nm under different humidity conditions using a tandem DMA setup. Both studies revealed a shrinkage with relative humidity conditions below the deliquescence threshold for dry sodium chloride particles. The cut-off diameter of the used TSI 3776 UCPC is at 2.5 nm according to the manufacturer at standard temperature settings. Therefore, we were aiming at studying the size range around the UCPC cut-off diameter using a tandem DMA setup to investigate the shrinkage of NaCl particles when exposed to a defined RH (the setup is also shown in Figure 1 in the comments of the second reviewer). Due to the low particle concentrations below 4.5 nm our measurements were limited to this particle size, but still the microstructural rearrangement yielded an attenuated decrease in size with decreasing particle diameter. Therefore, we assumed that the rearrangement or change in shape plays an important role for seed sizes >3 nm, but below the measured charge enhanced nucleation for sodium chloride particles influence the nucleation and growth process (C. Tauber et al., 2018). As a result, water molecules dissociate the NaCl cluster and a charge enhanced nucleation / growth leads to an enhanced activation.

The discussion around this shape effect would be greatly helped if data could be presented with the DMA run at the RH of interest. Why was not a recirculating pump / filter not used for some measurements? That would help the interpretation of the overall results and may lead to some sort of basis for a model description.

In order to test a humidity dependent change in particle size, we used a standard DMPS setup which has a filtered and dried (using Silica gel) sheath air loop. Our results confirmed the measurements conducted by Biskos et al. (2006) showing the shrinkage of sodium chloride particles in the presence of water vapor. Nevertheless, in the future we would like to conduct these measurements with humidified sheath air for comparison. Additionally, higher RH conditions could be used to investigate the influence of deliquescence on even smaller particles.

There is previous work on humidity effects for nanometer-sized sulfuric acid particles out of the Eisele-McMurry collaboration at NCAR. Also the O'Dowd group explored chemical effects and the activation of nano-particles. Those two studies were focused on pulse height analysis but the humidity effect explored here is integral to those experiments. I think the Donaldson group out of Toronto also discussed humidity effects in butanol CPCs. There are probably others and they should be cited. How would the PSM (Seinfeld, Kulmala etc.) instrument data be affected? How about alternate condensing fluids like diethylene glycol or FC43

(the latter used on aircraft campaigns by Brock and co-workers)?

We acknowledge the well-justified comment and thank the reviewer for making us aware of the pulse height analysis studies. The pulse height analysis conducted by D. R. Hanson et al. (2002) for sulfuric acid particles reveals a strong chemical composition and water vapor dependence. The size resolved chemical composition measurements of nanoparticles from reactions of sulfuric acid with ammonia and dimethylamine, investigated by H. Chen et al. (2018), suggest that small, acidic and newly formed particles can affect the physiochemical properties and thereby enhance early particle growth. We recommend that in further studies the chemical composition of the generated particles in different charging states are investigated. We assume that the chemical composition and charging state are the driving forces of nucleation and growth in size range of the cut-off diameter of the used UCPC.

Based on solubility effects and the increased polarity of the working fluid due to the addition of water molecules, similar effects using different working fluids can be assessed by interpreting their chemistry. DEG is a well polarized molecule due to three oxygen atoms per DEG molecule. Adding water does not increase the overall polarity as much as in the case of butanol. NaCl particles are soluble in DEG as well. As a result, it can be inferred that such a shift in the cut-off diameter is expected to be smaller than in the case of butanol. The working principle of PSMs (turbulent mixing) establishes a highly dynamic environment that leads to an increased rate of particle activation even without the presence of water (P. J. Wlasits, 2019).

Perfluorcarbonates (Fluorinert, FC-43): These compounds consist of carbon chains with fluorine atoms instead of hydrogen atoms. These molecules have a low dipole moment. Due to the spherical structure and very electronegative atoms on the outside the overall surface of the molecule is slightly negatively polarized. Consequently, a shift in the cut-off diameter can be expected by using a mixture of Perfluorcarbonates and water. The overall polarity of the working fluid would almost exclusively be based on the dipole moment of water molecules. Also, the pulse height analysis measurements by D. R. Hanson et al. (2002) revealed a weak size change when using FC-43 as working fluid.

The authors should consider changing the language from inverse temperature to some-thing like non-congruent (with the Kelvin ....) temperature dependence. Inverse temperature to many physical scientist means a 1/T dependence. . .

We thank the reviewer for the comment and we will reformulate to opposite temperature trend.

The non-native English speaking authors have had difficulty translating their thoughts into English. Hard to follow their logic at times. More on this at a later time: wanted to get these major comments to the authors for discussion etc.

The manuscript will be revised concerning grammar and word order.

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