

Authors Response to the Reviewer Comments regarding the manuscript “Humidity effects on the detection of soluble and insoluble nanoparticles in butanol operated condensation particle counters” by Tauber et al.

Dear editor,

we appreciate the thoughtful comments by the two reviewers which have substantially helped to improve and clarify our manuscript. All comments have been considered and are explained in the detailed point-by-point answers.

Sincerely,

Christian Tauber on behalf of all co-authors

Reviewer: 1

General comments:

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.

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

Response:

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 soluble substances 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.

These changes have been included in the manuscript:

“Thus, number concentration measurements should be paired with chemical and/or hygroscopicity measurements to improve the assessment of the uncertainty. If these additional measurements cannot be conducted, the location of the measurement site should be considered for data interpretation. Especially when conducting studies in marine surroundings, at which sea spray is one of the contributing particle sources, special care should be taken during the data evaluation (Lawler et al., 2014; Zieger et al., 2017).”

A concerning factor as to whether these results apply to the atmosphere: Are there actually any nanometer-sized NaCl aerosol in the atmosphere?

Response:

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.

Response:

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.

Response: These changes have been included in the manuscript:

“In order to test a humidity induced change in particle size, we used a standard DMPS setup, which has a filtered and dried (using Silica gel) sheath air loop. The corresponding setup schema can be found in the supporting information (Figure S3). 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) ?

Response:

We acknowledge the well-justified comment and thank the reviewer for making us aware of the pulse height analysis studies.

These changes have been included in the introduction section:

“In addition, pulse height analysis conducted by Hanson et al. (2002) for sulfuric acid particles revealed a strong dependence on chemical composition and water vapor. The size resolved chemical composition measurements of nanoparticles from reactions of sulfuric acid with ammonia and dimethylamine, investigated by Chen et al. (2018), suggest that small, acidic and newly formed particles can affect the physicochemical properties and thereby enhance early particle growth. This indicates a chemical cluster composition and working fluid dependence which results in a different activation behavior at the lower detection limit of the used CPC.”

These changes have been included in the results and discussion section:

“In general, 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 different particle solubilities are present in the atmosphere – these uncertainties of 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 for 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 and the source region of the seed particles 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.

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. Diethylene glycol (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.

Working fluids like perfluorcarbonates (Fluorinert, FC-43) 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 Hanson et al. (2002) revealed a weak size change when using FC-43 as working fluid. In fact, the interaction between the NaCl seeds and the water molecules will be persistent if only the working fluid gets changed. To remove the influence the carrier gas should be kept dry. In case the RH cannot be kept completely dry or only dry below a certain threshold value, the effect on a change in cut-off size should be considered in the data analysis. Especially at measurement sites located near the sea or at changing/high RH, which is the case for most regions.”

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

Response:

We thank the reviewer for the comment and reformulated 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.

Response:

The manuscript has been revised concerning grammar and word order.

Reviewer: 2

General comments:

Summary: *The paper demonstrates a humidity dependence on NaCl activation using a butanol CPC, where increasing humidity decreases the activation cut-size, while showing no such dependence with Ag particles. The measurement was performed with both continuous flow CPCs and the SANC. Due to the strong humidity-dependence of some particles, it is believed that ambient measurements could be activated at smaller sizes than their laboratory-controlled equivalent and care should be taken in assuming constant cut-sizes for butanol-based CPCs in ambient measurements of unknown composition.*

These results seem significant and interesting, but I think it could be reorganized to better integrate, introduce, and motivate each experiment's contribution to the objective. Some experiments are not fully motivated of their potential significance until the results section.

The abstract/intro is missing a significant section of the paper regarding charge effect. Poor humidity sensor selection for a paper on targeting humidity effects. Sensor uncertainties need to propagate through to resulting figures (e.g. Figure 4).

Response:

A paragraph in the introduction for the charge effect was added in the updated manuscript. The shrinkage measurements in Figure 4 were conducted with SHT75 sensors, with an accuracy of +/- 1.8% and with a HMI38 Humidity Data Processor with a HMP35E probe, with an accuracy of +/- 2.0%. For the sake of readability uncertainties were not included in Figure 4 in the final version of the manuscript. The corresponding uncertainties are discussed in the figure caption instead.

Would a working fluid such as Fluorinert counteract the humidity dependence of NaCl activation, or would the NaCl still uptake water and nucleate more easily with humidity? Practical solutions and guidelines for scientists would be helpful.

Response:

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. As a result, 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. In fact, the interaction between the NaCl seeds and the water molecules will be persistent if only the working fluid gets changed. To remove the influence the carrier gas should be kept dry. In case the RH cannot be kept completely dry or only dry below a certain threshold value, the effect of a change in cut-off size should be considered in the data analysis, especially at measurement sites located near the sea.

Major Comments: *The citations provided, on nucleation for example (P2 L5), should credit the work from previous authors. Also, heterogeneous nucleation mechanisms needs to include more sources than Wang et al. 2013. In general, the sources need to be expanded to include the major pioneers of the subjects. If the experiments were already performed with propanol in Schobesberger et al., why would a different behavior with butanol be expected? The difference between the papers, aside from changing the working fluid, should be highlighted.*

Response:

We acknowledge the well-justified comment on the citations of heterogeneous nucleation mechanism and included them in the updated manuscript. We were not expecting a different behavior. Initially the temperature dependence found by Schobesberger et al. (2010) was used to explain the enhanced detection efficiencies for NaCl found during the laboratory measurements. During the measurements it was found that the relative humidity dependence was stronger than the temperature dependence. Schobesberger et al. (2010) focused on the temperature dependence and compared it to different theoretical approaches like Fletcher theory. In this work we focused on the deviating activation behavior of butanol-based CPCs. The deviating activation behavior is caused by the temperature settings and by increased RH levels.

Figure 1 does not include control system mechanism for RH. The paper focuses on humidity as a primary variable, but not much detail was provided on how it was varied and controlled. Is RH controlled with a feedback loop to account for transients through-out the experiment? If RH is the main variable of interest, its introduction to the system and control should not be glossed over.

Response:

Figure 1 was moved into the supplemental materials. In the revised manuscript it was replaced by the Figure 1 shown below.

These changes have been included in the manuscript:

“Accordingly, the carrier gas was humidified by passing it through a diffusion type humidifier (see Figure 1). The relative humidity of the carrier gas was monitored and recorded throughout every measurement. The deviation of the recorded values was always below $\pm 1\%$ which is below the sensor accuracy.”

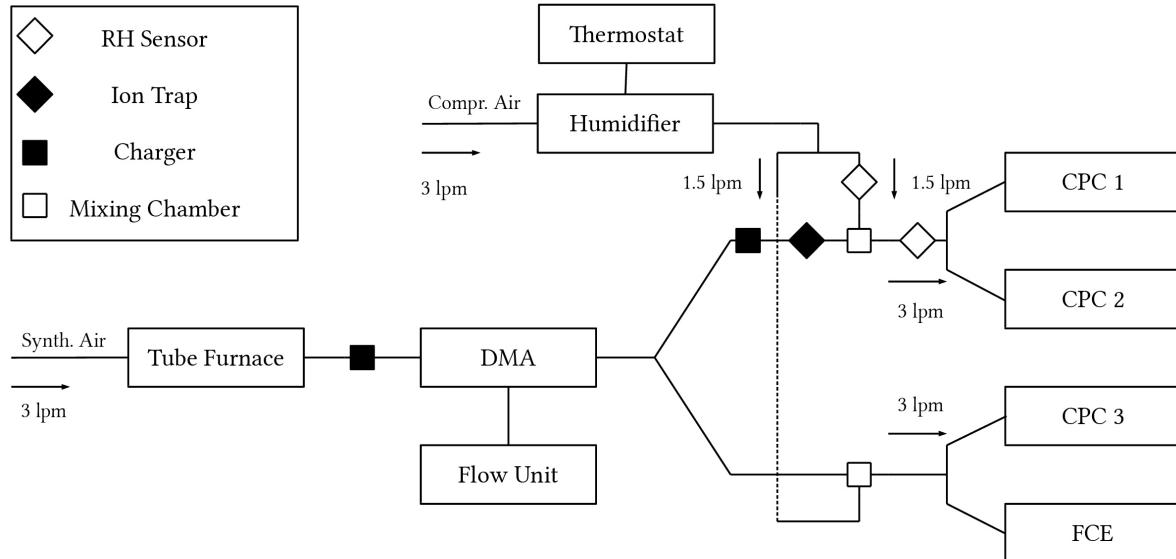


Figure 1. The experimental setup for evaluating the relative humidity dependent counting efficiency of continuous flow type CPCs (TSI 3776 UCPC), which was measured relative to a Faraday Cup Electrometer (FCE).

Honeywell sensors mentioned are crude (accuracy +/- 3.5%, hysteresis 3%, repeatability +/- 0.5%, etc.). These uncertainties need to be reflected in the figures.

Response:

The humidity measurements were conducted with two different humidity sensors. The cut-off diameter measurements were conducted with the Honeywell sensors. Due to the accuracy of +/- 3.5% the minimal RH difference between two measurements was 10%. The shrinkage measurements were conducted with SHT75 sensors with an accuracy of +/- 1.8%, hysteresis 1%, repeatability +/- 0.1% and with a HMP35E probe with an accuracy of +/- 2.0%. In the final version of the manuscript the error bars were not included in Figure 4 for improved readability. Uncertainties will be discussed in the figure caption.

Regarding the counting efficiency experiment (P4), each TSI CPC can have a unique counting efficiency based on laser age, optics cleanliness, alignment, etc. Characterizing the effect of CPC deltaT on nucleation effectiveness using 3 different CPCs does not seem substantial enough, as each CPC could have a different counting efficiency at the same temperature. It would have been preferable to compare one CPC and repeat the experiment 3 times, so the additional factors mentioned above are constrained. Otherwise, it would need to be stated that the 3 CPCs have been normalized to one another for each of the deltaTs (or proven operation is identical).

Response: These changes have been included in the manuscript:

“In total, about 400 detection efficiency curves were recorded. To rule out any dependence of the individual activation behavior of different CPCs, measurements involving one single CPC set to all three temperature settings one after another, and measurements involving three CPCs that were all set to one specific setting, have been performed. Based on these measurements, the maximum error linked to the individual activation behavior was calculated to be at the highest at 8.1%.”

Figure 2 and 3 are chosen as exemplary measurements for different temperature settings and CPCs at the same T settings (C. Tauber et al., 2019) and can be found in the supplemental material.

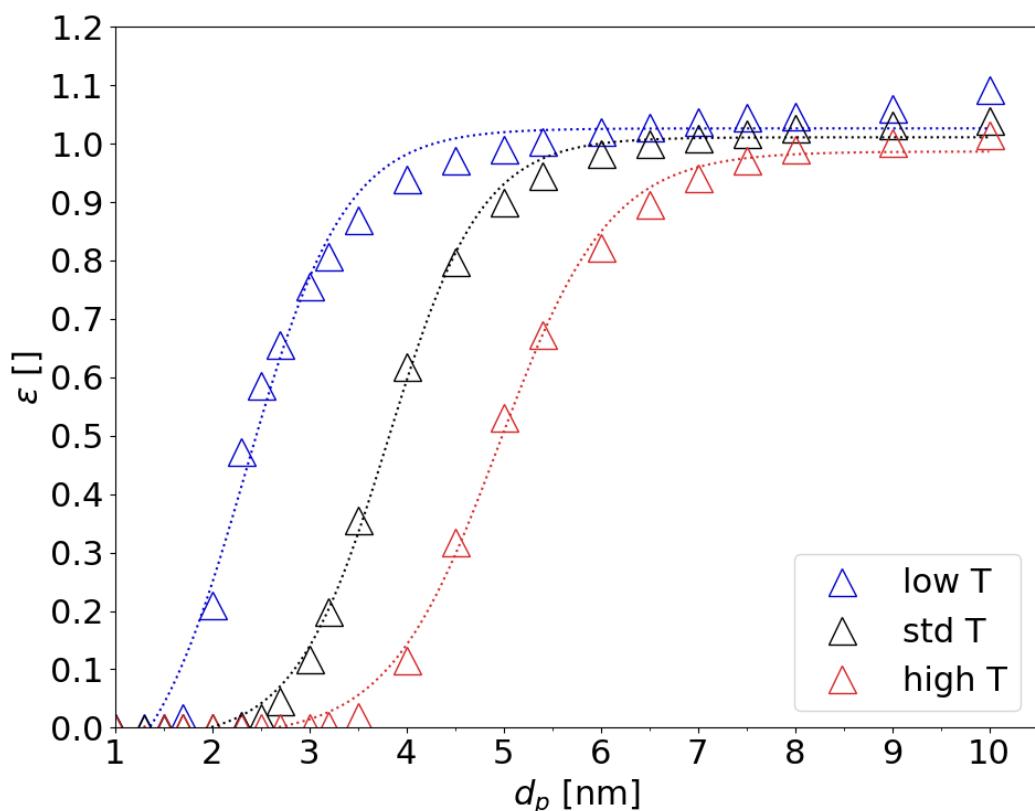


Figure 2. NaCl positive with 10% RH, all curves were recorded with the same CPC.

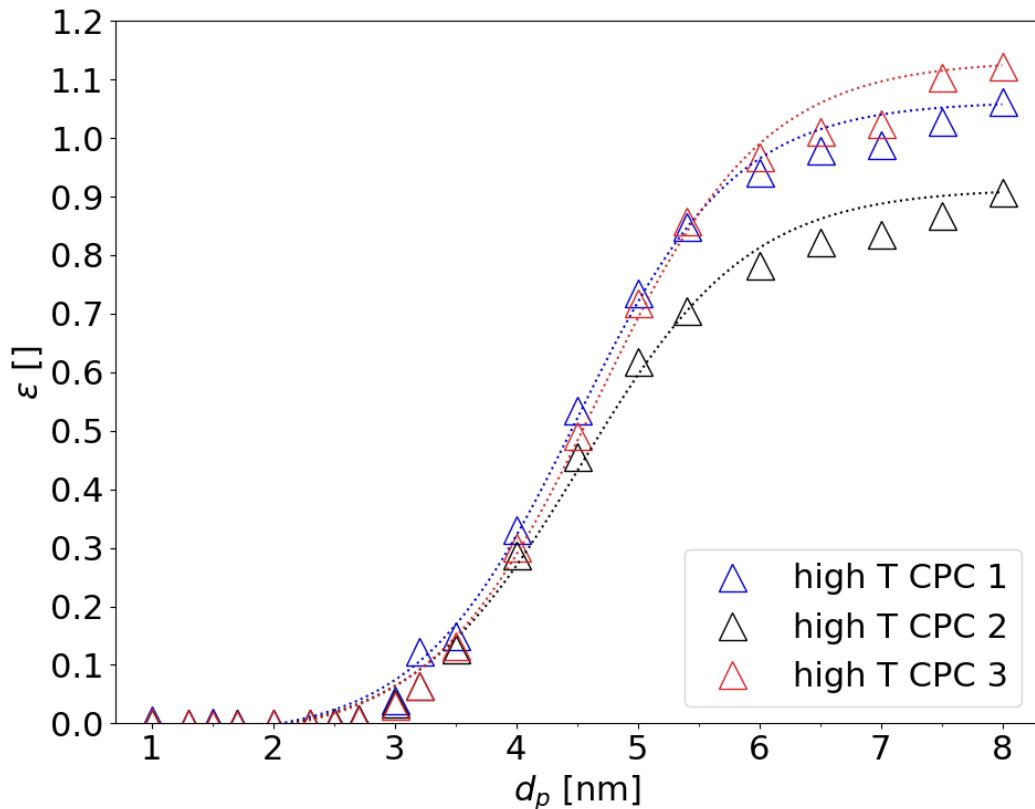


Figure 3. NaCl negative with 0% RH, all curves were recorded with different CPCs but at constant temperature settings.

The charge effect isn't addressed in the abstract or introduction/background and seems significant to the NaCl activation. The inclusion of this experiment is good, but it feels like it came only at the result of Section 3.1, and didn't have its own proper introduction to motivate why it's included.

Response:

We thank the reviewer for making us aware of the leak in the introduction section. In the updated manuscript we added an additional paragraph on the charge dependence to the introduction.

These changes have been included in the manuscript:

“In a recently published paper by Tauber et al. (2018), it has been shown that the presence of monoatomic ions significantly lowers the energy barrier for the heterogeneous nucleation of n-butanol. It is known from previous studies that ion induced nucleation is highly affected by the chemical structure of the condensing vapor and seed ion properties like charge state (Iida et al., 2009; Kangasluoma et al., 2016). This process takes place in the sub-3 nm size range at which condensation-based nanoparticle detection methods have their lower detection limit. Thereby the initial charge state of aerosol particles with diameters within this size range can influence the detection efficiency.”

Minor Comments: P1 L14-22: This paragraph seems irrelevant to the focus of the paper goals and losing it would not detract from the message. The overview seems a little vague, when it would benefit with a background more targeted to the objective.

Response:

We removed this paragraph and added an introduction paragraph on the charge dependence / effect.

Commas must be added in sentences using passive voice. This is done with some, but not all sentences and must be corrected throughout.

Response:

We reviewed the manuscript to correct for that.

Simplify wordy sentences throughout: e.g. P2 L4: “This process is called nucleation and arises...” could simplify to “This process of nucleation arises...”; and P2 L18.

Response:

This change has been included in the updated manuscript.

P2 L7: Remove “a” to make CCN plural to agree with your verb and that you used “nuclei” instead of “nucleus”, i.e. “...nanometer-sized particles contribute as cloud condensation nuclei (CCN).”

Response:

This change has been included in the updated manuscript.

P2 L15-17: You describe deliquescence and efflorescence without using the term for the mechanism.

Response:

This has been included in the updated manuscript.

P2 L 20: Subject-verb agreement; “One technique...is CPCs”, not “are”.

Response:

This change has been included in the updated manuscript.

Humidity effects on the detection of soluble and insoluble nanoparticles in butanol operated condensation particle counters

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Abstract. In this study the impact of humidity on heterogeneous nucleation of n-butanol onto hygroscopic and nonabsorbent charged and neutral particles was investigated using a fast expansion chamber and commercial continuous flow type condensation particle counters (CPCs). More specifically, we measured the activation probability of sodium chloride (NaCl) and silver (Ag) nano-particles by using n-butanol as condensing liquid with the size analyzing nuclei counter (SANC). In addition, the

5 cut-off diameter diameters of regular butanol based CPCs for both seed materials was under different charging states were measured and compared to SANC results. Our findings reveal a strong humidity dependence of NaCl particles in the sub-10 nm size range since the activation of sodium chloride seeds is enhanced with increasing relative humidity. In addition, negatively charged NaCl particles with a diameter below 3.5 nm reveal a charge enhanced activation. For Ag seeds this humidity and charge dependence was not observed, underlining the importance of molecular interactions between seed and vapor molecules.

10 Consequently, the cut-off diameter of a butanol based CPC can be reduced significantly by increasing the relative humidity. This finding suggests that cut-off diameters of butanol CPCs under ambient conditions are likely smaller than corresponding cut-off diameters measured under clean (dry) laboratory conditions. At the same time, we caution that the humidity dependence may lead to wrong interpretations if the aerosol composition is not known.

1 Introduction

15 Aerosol particles are present in the atmosphere in various kinds. Since the size of these particles range from a few nanometers up to 100 μm the detection method has to be carefully chosen. Typically, aerosol particles are measured in number concentration and mass concentration. The current state-of-the-art technology of real-time aerosol mass concentration measurements is based on acoustic and electromechanical sensors (Soysal et al., 2017). On the other hand, number concentration measurements are conducted using optical and electrical aerosol instruments. Ultrafine particles which have diameters less than 100 nm are known to increase the risk of respiratory and cardiovascular diseases (Saghafifar et al., 2009; Kaiser, 2005; Pope et al., 2009).

20 The mass contribution of ultrafine particles is small and therefore the number density of particles is suggested to be more related to adverse health effects (Nel, 2005). As a consequence, number concentration measurements are preferred in health-related studies, clean room technology, as well as in cloud formation and climate related studies (Saghafifar et al., 2009).

In the atmosphere nano-particle formation by gas-to-particle conversion has been observed in a variety of locations and conditions (Kulmala et al., 2004). On a global scale, it is seen as an important source controlling the number size distribution of atmospheric aerosols (Kulmala et al., 2014). Thereby, a phase transition from the gaseous to the liquid or solid state occurs in the presence of supersaturated vapors. This process is called nucleation and of nucleation arises homogeneously from gas molecules only, or heterogeneously by the formation of vapor clusters on preexisting particles (Strey et al., 1986); (Winkler et al., 2008b); (Kangasluoma et al., 2016); (Ferreiro et al., 2016); (Tauber et al., 2018). These nano-particles then can grow up to a size at which they act as a cloud condensation nuclei (CCN) (Spracklen et al., 2008; Merikanto et al., 2009). Thereby nanometer-sized particles contribute to the indirect radiative forcing, thus influencing the Earth's climate (IPCC, 2013).

Heterogeneous nucleation in the atmosphere takes place for seed particles and vapor molecules of different chemical composition. Aerosol particles acting as seeds in the heterogeneous nucleation process have different physicochemical surface properties such as charging state, wettability, shape or size. Interactions between the seed and the vapor molecules as well as solubility play an important role (Kupc et al., 2013; McGraw et al., 2012, 2017). Atmospheric aerosol can contain hygroscopic salts and is therefore sensitive to relative humidity which can contribute to a phase transition within the aerosol particle.

A highly hygroscopic and well characterized example is sodium chloride (NaCl) which mainly originates from sea spray (Biskos et al., 2006; Krämer et al., 2000; Clarke et al., 2003; Lawler et al., 2014; Zieger et al., 2017). Water vapor strongly influences the phase of the hygroscopic NaCl particles which under dry conditions exhibit a solid crystalline structure. At high relative humidity (RH), salt particles take up water and form a saline droplet with increased volume which affects its physical, chemical and optical properties. In contrast to increasing RH, aqueous saline aerosol particles shrink with decreasing relative humidity. Thereby the water evaporates and the seed crystalizes (Martin, 2000; Biskos et al., 2006).

In a recently published paper by Tauber et al. (2018), it has been shown that the presence of monoatomic ions significantly lowers the energy barrier for the heterogeneous nucleation of n-butanol. It is known from previous studies that ion induced nucleation is highly affected by the chemical structure of the condensing vapor and seed ion properties like charge state (Iida et al., 2009); (Kangasluoma et al., 2016). This process takes place in the sub-3 nm size range at which condensation-based nanoparticle detection methods have their lower detection limit. Thereby the initial charge state of aerosol particles with diameters within this size range can influence the detection efficiency.

In the atmosphere usually more than a single species of vapor molecules contributes to the vapor-liquid nucleation. Both processes, gas-to-particle conversion and the existence of insoluble particles in the atmosphere, can initiate heterogeneous nucleation processes (Wang et al., 2013). One (Kulmala et al., 2004; McMurry et al., 2005; Kuang et al., 2010, 2012; Wang et al., 2013).

A commonly used technique to measure preexisting particles in the atmosphere are is Condensation Particle Counters (CPCs), which are oftentimes using often use n-butanol as working fluid (McMurry, 2000). However, under ambient conditions significant amounts of water vapor usually enter the CPC and can modify the detection behaviour of the CPC. Previous studies on binary heterogeneous nucleation of n-propanol-water vapor mixtures on sodium chloride (NaCl) particles indicated a decrease of the activation barrier and reported a soluble-insoluble transition in the particle activation behaviour (Petersen et al., 2001).

Butanol is chemically similar to propanol and therefore the process of heterogeneous nucleation of n-butanol and water vapor

on nanometer sized particles is of high relevance in ambient nanoparticle characterization studies. In addition, pulse height analysis conducted by Hanson et al. (2002) for sulfuric acid particles revealed a strong dependence on chemical composition and water vapor. The size resolved chemical composition measurements of nanoparticles from reactions of sulfuric acid with ammonia and dimethylamine, investigated by Chen et al. (2018), suggest that small, acidic and newly formed particles can 5 affect the physicochemical properties and thereby enhance early particle growth. This indicates a chemical cluster composition and working fluid dependence which results in a different activation behavior at the lower detection limit of the used CPC.

Over the last years various studies investigated the onset saturation ratio and the nucleation temperature for different seeds and vapors. These studies include measurements by Chen and Tao (2000) for water on SiO₂ and TiO₂, and Schobesberger et al. (2010) for n-propanol on silver (Ag) and sodium chloride seeds. All studies show that the expected temperature trend agrees 10 with theory, except for the nucleation of n-propanol on NaCl particles. In this specific case a-reversed-an opposite temperature trend of the onset saturation ratio compared to the Kelvin equation in the temperature range from 262 K to 287 K was recorded (Schobesberger et al., 2010). Despite the common use of butanol as working fluid for the detection of ambient nanoparticles surprisingly little nucleation research has been done in the sub-10 nm size range. Here Hence, we investigate heterogeneous 15 nucleation of n-butanol vapor on differently sized seeds depending on relative humidity, charge state and nucleation temperature. In contrast to Schobesberger et al. (2010), we focus on the deviating activation behavior of butanol-based CPCs in this work. We aim at getting a better understanding of the effect of RH and initial charging states on the nucleation process in CPCs with the focus on sub-5 nanometer particles. Thereby the relative humidity effect and charge dependence on the lower particle 20 detection limit can be analyzed. The results help to improve the understanding of heterogeneous nucleation of n-butanol vapor on soluble and insoluble seeds. By that the acting mechanism during the nucleation process can be analyzed and used to explain changes of the counting efficiencies in commercial CPCs (Ankilov et al., 2002).

2 Experimental Section

We examined the nucleation probability and counting efficiency of n-butanol based CPCs as shown schematically in Figure 1 and Figure S1 in the supporting information. Ag and NaCl particles were generated in a tube furnace (Scheibel and Pors- 25 tendörfer, 1983) which was supplied with synthetic air (ALPHAGAZ 1 AIR, >= 99.999% (5.0), Air Liquide) or particle-free dry compressed air. The flow carrying the polydisperse aerosol was kept constant at 3 L/min through the Americium 241 (Am- 241) charger and the nano differential mobility analyzer (nDMA) for both experimental approaches. By applying positive or negative voltage to the nDMA a monodisperse negatively or positively charged particle fraction was selected. By placing an Am-241 charger either at the Size Analyzing Nuclei Counter (SANC) or the CPC inlet the size selected particles were neutralized. Subsequently, ions that form inside the charger were removed using an ion trap. An adjustable well-defined flow of 30 humid air joined the aerosol flow after the nDMA in order to vary the humidity of before the CPC inlet flow. Accordingly, the carrier gas was humidified by passing it through a diffusion type humidifier (see Figure 1). The relative humidity of the carrier gas was monitored and recorded throughout every measurement. The deviation of the recorded values was always below $\pm 1\%$ which is below the sensor accuracy. Two humidity sensors (HIH-4000-004, Honeywell) monitored the humidity of the aerosol

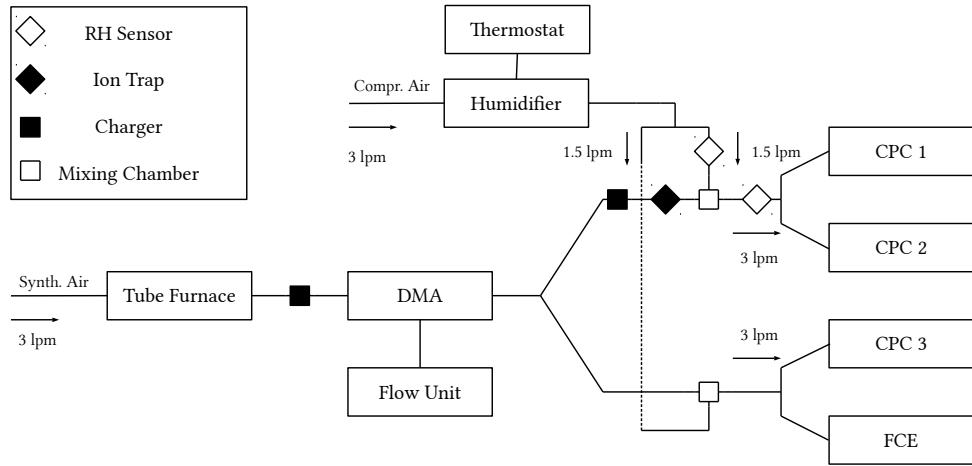


Figure 1. The experimental setup for evaluating the supersaturation and nucleation temperature with the SANC and the relative humidity dependent counting efficiency measurements of a continuous flow type CPCs (TSI 3776 UCPC), which was measured by operating relative to a Faraday Cup Electrometer (FCE) in parallel (Wlasits, 2019).

flow before and after the injection of the humid flow. The amount of water vapor during the counting efficiency measurements was kept constant.

Measurements of heterogeneous nucleation of n-butanol at nucleation temperatures ranging from 270 K to 292 K were carried out with the SANC (Wagner et al., 2003). To this end, monodisperse particle fractions were mixed with a carrier gas flow of 5 L/min containing n-butanol vapor and led into the expansion chamber of the SANC. N-butanol vapor was added to the system by controlled injection using a syringe pump, followed by quantitative evaporation of the liquid beam in a heating unit (Winkler et al., 2008a). As a result, the well-defined and nearly saturated binary vapor-air mixture together with size selected, neutralized monodisperse seed particles from the nDMA was passed into the temperature controlled expansion chamber. Vapor supersaturation was achieved by adiabatic expansion, and the number concentration of droplets nucleating on the seeds was measured with the Constant Angle Mie Scattering (CAMS) method (Wagner, 1985). Based on the CAMS-method a one to one correlation between the time dependent measured scattered light flux under a constant angle and the calculated scattered light flux as a function of droplet size can be established. Thus, we are able to determine the growth curve of the growing droplets which can be compared to theoretical calculations from a condensation model. Thereby, the saturation ratio can be verified with an accuracy of 2-3 percent. Thus, the radius and the number concentration of the growing droplets could be determined simultaneously. By varying the chamber temperature and the pressure drop in the expansion chamber, different nucleation conditions were analyzed. The nucleation or activation probabilities were measured with the SANC/CAMS method

Table 1. Temperature settings of the three TSI 3776 UCPCs used in this study in parallel.

settings	low T [°C]	standard T [°C]	high T [°C]
condenser	1.1	10.0	18.9
saturator	30.1	39.0	47.9
optics	31.1	40.0	48.9

(Wagner et al., 2003). To evaluate the onset saturation ratio, which corresponds to a nucleation probability value of $P = 0.5$, the experimental data were fitted with a two-parameter fit function (Winkler et al., 2016).

In addition to the SANC measurements, the counting efficiencies of three ultrafine continuous flow type CPCs (Model UCPC 3776, TSI Inc., Minneapolis, USA), which temperature settings were changed over a range of 18 degrees, were measured. In 5 contrast to the SANC, the supersaturation is obtained by saturating a laminar flow and subsequently cooling the aerosol together with the saturated flow in the condenser. Both methods lead to heterogeneous nucleation and condensation of n-butanol vapor on the aerosol particles due to a temperature decrease~~reduction~~. Thereby the particles grow to a size at which they can be detected optically. To measure the detection efficiency of the TSI UCPCs, the aerosol flow subsequent to size classification was 10 symmetrically split. The aerosol was passed to three CPCs ($N_{CPC,1-3}$), each operating at different temperature settings (see Table 1), and to the Faraday Cup Electrometer (FCE) (N_{FCE}), which was operated in parallel. Thereby the counting efficiency was determined relative~~relatively~~ to a FCE (Model 3068B Aerosol Electrometer, TSI Inc., Minneapolis, USA). Hence the detection efficiency~~efficieney~~ η of a UCPC can be determined by comparing the number concentration of the CPC $N_{CPC,1-3}$ and the total number concentration N_{FCE} as follows according to the following relation:

$$\eta = \frac{N_{CPC,1-3}}{N_{FCE}}. \quad (1)$$

15 By operating the CPCs at different temperature settings we were able to analyze the detection efficiency with various peak super saturation ratios (Tauber et al., 2019). The particle detection efficiency mainly depends on the activation probability, which is primarily a function of supersaturation and particle diameter (Barmpounis et al., 2018). By conducting detection efficiency measurements the cut-off diameter is determined, which represents. The cut-off diameter corresponds to the mobility diameter where~~at which~~ 50% of the particles can be~~are~~ counted in a CPC.

20 3 Results and Discussion

3.1 Temperature and Humidity Effects

Here we report In this chapter we discuss the measurements of the onset saturation ratio of n-butanol depending on nucleation temperature and humidity with the SANC. The heterogeneous nucleation probability (P) for different seeds and seed properties in the size range of 2.5 to 10.5 nm mobility diameter was investigated. The heterogeneous nucleation probability

represents the number concentration of activated seeds normalized to the total number concentration of the aerosol. It depends on the saturation ratio which is given by the ratio of partial vapor pressure divided by the equilibrium vapor pressure at the corresponding temperature after expansion (nucleation temperature T_{nuc}). Measurements were conducted at constant T_{nuc} by varying the vapor amount and keeping the pressure drop constant. In a recent study we have shown that with reduced nucleation 5 temperatures the onset saturation ratio needed to activate a certain Ag particle size increases (Tauber et al., 2019). This is in line with classic Kelvin predictions (Thomson, 1871). To investigate the impact of RH on heterogeneous nucleation probability the Ag measurements were complemented by NaCl seeds. The resulting onset saturation ratios depending on the nucleation temperatures are shown in Figure 2. Clearly, the required saturation ratio to activate a certain particle size is always lower for 10 Ag particles compared to NaCl particles. Heterogeneous nucleation of n-butanol vapor on NaCl and Ag aerosol particles shows a remarkably different behavior. An inverse opposite temperature trend for NaCl seeds was identified when compared to the Kelvin prediction, except for the smallest sodium chloride particles with a mobility diameter of 2.5 nm. Such a trend was not 15 found for silver nano-particles.

This finding is consistent with already published results from Schobesberger et al. (2010) for n-propanol, where an inversed opposite temperature trend for NaCl but not for Ag seeds could be observed. To rule out any humidity effects, the sheath 20 air of the nDMA was monitored with using a commercial relative humidity sensor during the measurements. Thereby an accumulation of water in the used silica gel dryer of the sheath air loop could be recorded. The water aggregation in the drier, originating from the compressed air supply, reached values up to 10% RH at 22°C room temperature. As a consequence, the carrier gas supplement for the experiment was changed from dried and filtered compressed air to synthetic airand additional. Additional 25 measurements were performed with a relative humidity $\text{RH} < 2.5\% < 3.5\%$.

20 The experimental values are shown in Figure 3. In Figure 3 the experimental values for neutral sodium chloride seeds are shown and listed in Table Tables S5-S9 of the supporting information for both considered aerosol species. The needed necessary onset saturation ratio for activating "dry particles" of a certain size is at the same value as for "high" RH values (< 10%) or (with one exception) increased for dry measurements (RH $\text{RH} < 2.5\% < 3.5\%$). In other words, the additional small amount of 25 water vapor during the measurements decreases the energy barrier which has to be overcome to activate a sodium chloride nano-particle with n-butanol in the observed size range. This finding suggests that already even small contaminations of water vapor can influence the heterogeneous nucleation of butanolwhich, a finding that agrees with already published studies for n-propanol-water mixtures on Ag and NaCl particles (Wagner et al., 2003).

For the heterogeneous nucleation of n-butanol on silver seeds no decreased decrease of the onset saturation ratio was observed during due to the presence of water vapor. The inverse was observed. The opposite temperature dependence for NaCl 30 and synthetic air as carrier gas (blue symbols in Figure 3) vanishes for small mobility diameters (< 3.5 nm), but particle sizes above 3.5 nm still follow the unusual temperature dependence. This indicates that sodium chloride particles act differently in the observed size range. It seems that NaCl seeds at sizes below ~ 3.5 nm are less prone to dissolution or restructuring effects. As a result, the nucleation of n-butanol on small NaCl seeds is comparable to silver clusters and the inverse. The opposite temperature vanishes and follows the Kelvin relation. One other Another remaining question is whether: Does the charge sign 35 during mobility selection has have an effect on the heterogeneous nucleation. Therefore heterogeneous nucleation? To answer

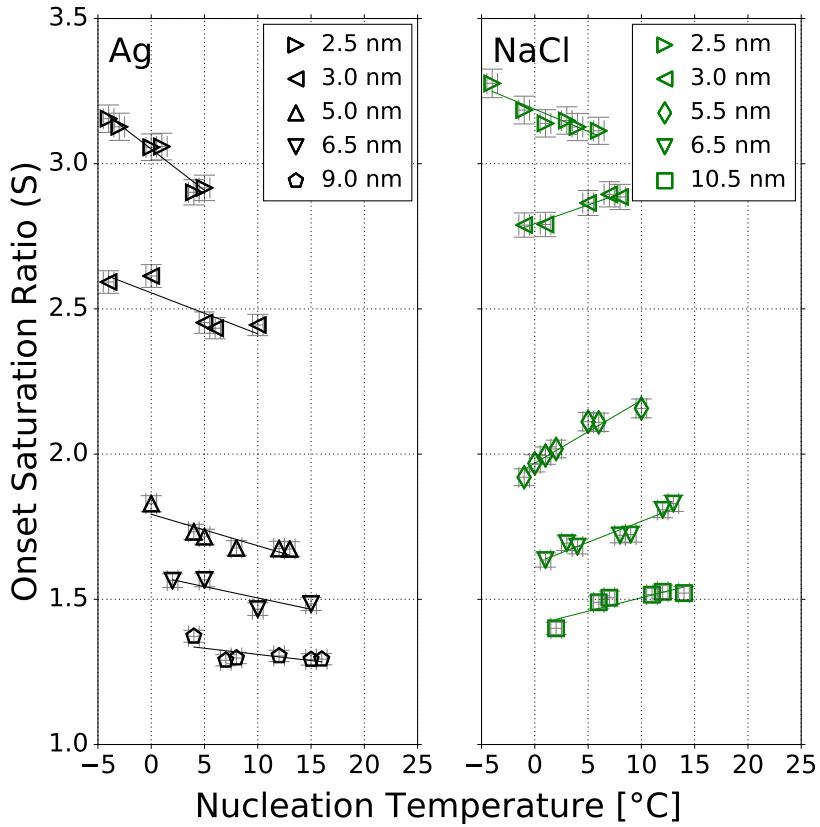


Figure 2. The onset saturation ratio versus nucleation temperature for neutral Ag (black) and NaCl (green) particles of different mobility equivalent diameters. With decreasing temperature the onset saturation ratio decreases for sodium chloride and increases for silver nanometer sized particles. Only the 2.5 nm NaCl seeds do not follow the [inverse opposite](#) temperature trend. Lines represent a linear fit of data to show the temperature dependence for NaCl and Ag seeds. The onset saturation ratio increases with decreasing seed size for both test aerosols.

[this question](#), additional measurements focusing on charge and humidity for NaCl particles in the corresponding nanometer range were conducted.

3.2 The Influence of Charge and Particle Restructuring Effects

To investigate the charge effect on heterogeneous nucleation of n-butanol vapor on silver and sodium chloride particles the 5 neutralizer and ion-trap in front of the expansion chamber (see Figure [4S1](#)) were removed. Thereby the seeds were positively or negatively charged, depending on the applied voltage to the nDMA. Nucleation studies were conducted with constant nucleation temperatures but varying charge state of the aerosol [with using](#) synthetic air as carrier gas. For positively charged silver particles no charge dependence on heterogeneous nucleation was found. However, NaCl seeds show a charge

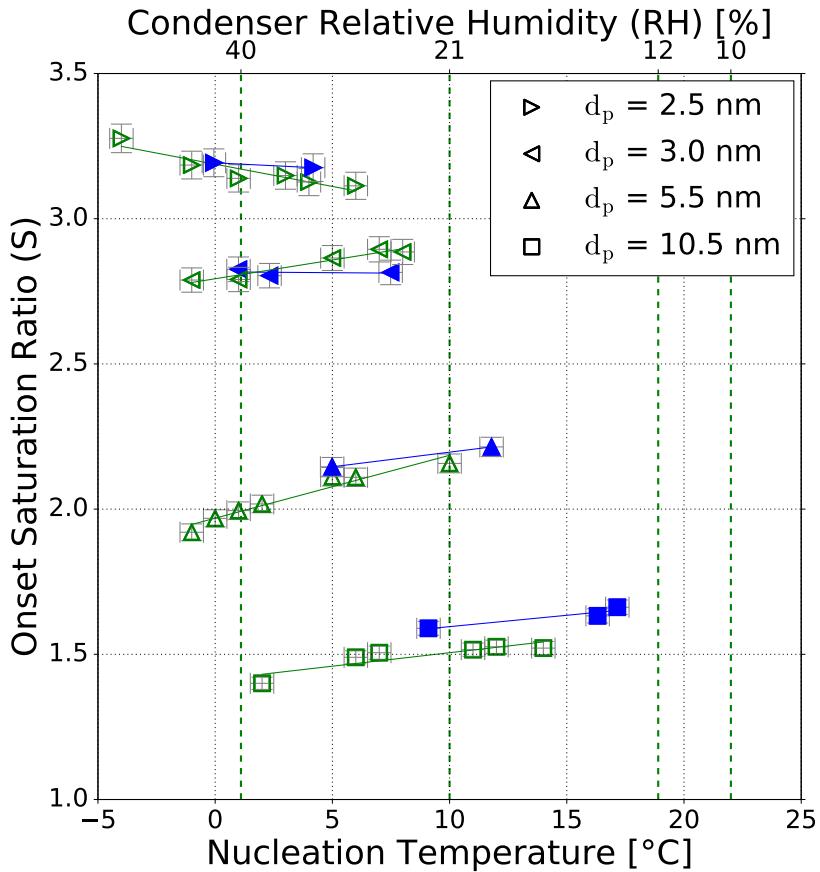


Figure 3. The onset saturation ratio versus nucleation temperature for NaCl particles of different mobility equivalent ~~diameter~~diameters. The green symbols show the onset saturation values recorded with relative humidity values $\leq 10\%$ and the blue symbols represent measurement values when the RH was $< 2.5\% < 3.5\%$. The green dashed vertical lines represent the calculated relative humidities at the corresponding preset condenser temperature (see Table 1) with a starting value of 10% RH at 22°C . The increased relative humidity inside the condenser of a TSI 3776 UCPC for reduced nucleation temperatures is shown ~~which~~ and will be discussed in the counting efficiency measurements section.

~~enhancement~~dependence, especially below 5 nm. As listed in Table 2 the necessary onset saturation ratio for neutral and positively charged silver particles is below the NaCl values, and no charge enhancement was found. Negatively charged Ag particles could not be fully investigated due to technical problems with the SANC at the end of the measurement run. Kangasluoma et al. (2016) conducted measurements using tungsten oxide, ammonium sulfate and tetraheptylammonium bromide nano clusters of 5 different charge states to determine the counting efficiency. During their studies a charge ~~enhancement of~~enhanced particle activation was observed similar to our findings regarding the NaCl measurements.

Table 2. SANC experimental results for the onset saturation ratio for neutral (n), positively (+) and negatively (-) charged particles. D_p is the mean mobility equivalent diameter, σ_g the mean geometric standard deviation and S_{onset} the onset saturation ratio.

D_p [nm]	σ_g	Ag ($RH < 2.5\%$)			NaCl ($RH < 2.5\%$)		
		S_{onset}	S_{onset}	S_{onset}	S_{onset}	S_{onset}	S_{onset}
		n	+	-	n	+	-
2.5	1.073	3.10	3.07	-	3.19	3.20	3.04
3.0	1.070	2.48	2.48	-	2.81	2.72	2.64
3.5	1.067	2.33	2.33	-	2.60	2.54	2.47
5.5	1.065	1.85	1.85	1.83	2.21	-	2.20
9.0	1.068	1.34	1.36	-	-	-	-
10.5	1.067	-	-	-	1.64	1.66	1.63

It is known from prior research that NaCl aerosol particles, which are generated by evaporation and condensation in a tube furnace, undergo a structural change in the presence of water (Krämer et al., 2000; Biskos et al., 2006) or n-propanol (Petersen et al., 2001; Kulmala et al., 2001). As a consequence, the particles shrink in the presence of polar vapors. In order to test a humidity induced change in particle size, we used a standard DMPS setup, which has a filtered and dried (using Silica gel) sheath air loop. The corresponding setup schema can be found in the supporting information (Figure S3). Our results confirmed the measurements conducted by Biskos et al. (2006), showing the shrinkage of sodium chloride particles in the presence of water vapor. This shrinkage was also investigated in our study for n-butanol and water and the. The experimental results for water are shown in Figure 4. We measured monodisperse NaCl aerosols with mobility diameters between 4.5 and 11 nm at relative humidities up to 50%. The shrinkage measurements in Figure 4 were conducted with SHT75 sensors, with an accuracy of $\pm 1.8\%$ RH and with a HMI38 Humidity Data Processor with a HMP35E probe, with an accuracy of $\pm 2.0\%$ RH. However, with decreasing mobility diameter, also the shrinkage becomes less. For example, an 11 nm NaCl particle exposed to 40% RH is shrinking by about 15% and a A 4.5 nm particle at 40% RH shrinks only by about 3%. Hence, the structural rearrangement for of particles below 5 nm is not as pronounced as for larger ones. This decrease in size for particles > 5 nm is a result of solvation on the surface of the NaCl particle caused by the presence of water vapor and thereby. Thereby a wet surface accrues (Castarède and Thomson, 2018). Due to this dissociation process and the resulting liquid surface the particle attracts more polar vapor molecules. In addition, the overall polarity of the working fluid of n-butanol and water mixture increases, due to the higher dipole moment of water (6.2×10^{-30} Cm) compared to n-butanol (5.8×10^{-30} Cm) (Reichardt and Welton, 2011). As a result, additional vapor molecules can more readily condense onto the seed aerosol. This mechanism could explain the resulting lower onset saturation ratio needed for NaCl seeds ≥ 3 nm as shown in Figure 3 for lower nucleation temperatures. As a consequence Consequently, by reducing the nucleation temperature the saturation vapor pressure decreases, leading to an increase in the saturation ratio for water (RH is increasing, see Figure 3, upper x-axis).

In summary, the SANC measurements allowed us to study the heterogeneous nucleation of n-butanol depending on the charge state, nucleation temperature and humidity of the carrier gas. Charge enhanced nucleation could be found for sodium

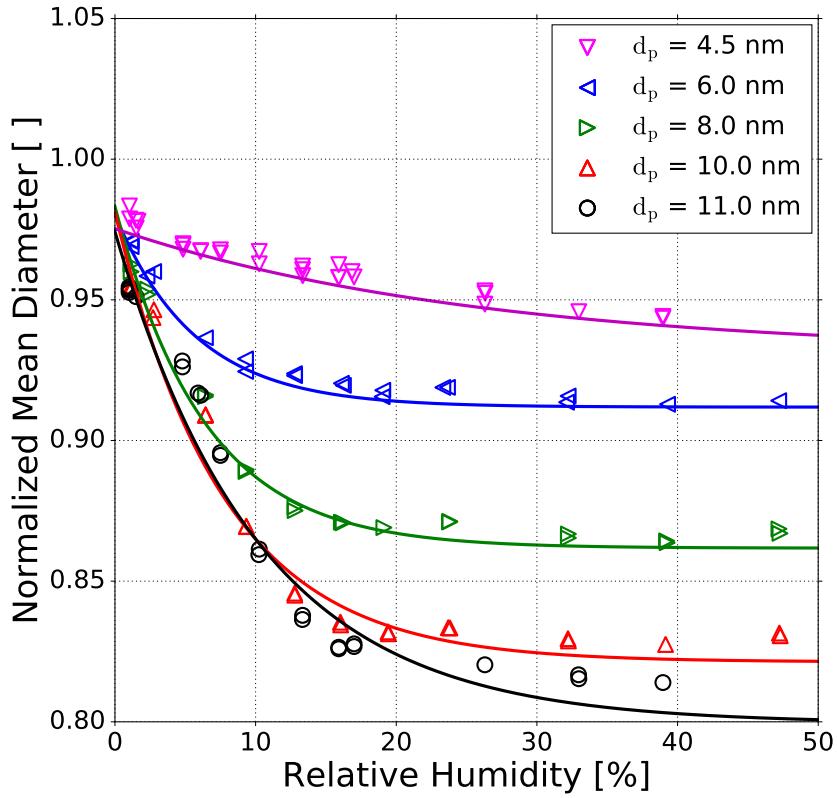


Figure 4. Normalized mean diameter of sodium chloride particles as a function of relative humidity which represents the shrinkage of NaCl seeds in the presence of water vapor. All sizes are mobility equivalent diameters. Each line represents a tentative three-parameter fit of an exponential decay. [The measurements were conducted with SHT75 sensors with an accuracy of \$\pm 1.8\%\$ RH and with a HMP35E probe with an accuracy of \$\pm 2.0\%\$ RH.](#)

chloride particles ≤ 3.5 nm, yet not for silver particles. By taking special care of the water vapor amount a humidity enhanced nucleation for sodium chloride seeds was found. Under dry conditions the observed [inverse opposite](#) temperature trend for NaCl seeds < 3.5 nm vanishes. For larger sodium chloride particles this trend is found to be persistent.

3.3 Counting Efficiency Measurements

5 [In addition, Complementing the SANC measurements we have performed](#) counting efficiency measurements at [variable different](#) condenser temperatures, but constant ΔT between saturator and condenser, [for a commercial n-butanol TSI 3776 UCPC, were performed](#). As a consequence, we were able to increase or decrease the saturation ratio profile as described by Tauber et al. (2019). The onset saturation ratio and nucleation temperature measured with the SANC for a classified monodisperse seed

Table 3. Calculated maxima of the CPC saturation ratio profiles S_{max} for low, standard and high temperature settings (Tauber et al., 2019), in comparision to the extrapolated S_{onset} as measured by the SANC.

d_p [nm]		NaCl neutral ($RH < 3.5\%$)				NaCl neutral ($RH < 10.0\%$)			
		2.5	3.0	3.5	5.5	2.5	3.0	3.5	5.5
T settings	S_{max}	S_{onset}	S_{onset}	S_{onset}	S_{onset}	S_{onset}	S_{onset}	S_{onset}	S_{onset}
low	4.3	3.18	2.81	2.65	2.10	3.17	2.80	-	1.99
standard	3.4	3.15	2.81	2.57	2.20	3.03	2.92	-	2.18
high	2.8	3.11	2.80	2.50	2.28	2.90	3.03	-	2.37

particle could be compared to the three different temperature settings of the condenser. The maximum value for the calculated saturation ratio profiles and the extrapolated S_{onset} for NaCl (partly extrapolated from the lines in Figure 2 and 3) under different humidity conditions at low, standard and high condenser temperatures are listed in Table 3. ~~Thereby~~ Thus, the ability to activate sodium chloride seeds in the ~~eutoff~~ cut-off range of a commerical UCPC could be analyzed. With increasing temperature the maximum saturation ratio (S) decreases. As a result, the detection efficiency is shifting to ~~bigger~~ larger particle sizes as shown in Figure 5.

For the verification of our findings we measured the cut-off diameter, charge and relative humidity dependence for the TSI 3776 UCPC at different temperature settings. By varying the temperature settings of the UCPC we were also able to measure under different condenser temperatures (see Table 1). For comparison, particle classification with the nDMA was always performed under dry conditions ($RH < 2.5\% \leq 3.5\%$), so that the structural change of the sodium chloride clusters does not influence the classification and the size of the generated aerosol. ~~After~~ Subsequent to the size selection, the particles were mixed with humidified air to reach RH values ranging from 0 to 40% as shown in Figure 1. Hence, we were able to vary the relative humidity with an accuracy of $\pm 2.5\% \pm 3.5\%$ by measuring the humidity before and after the mixing zone. ~~In total, about 400 detection efficiency curves were recorded. To rule out any dependence of the individual activation behavior of different CPCs, measurements involving one single CPC set to all three temperature settings one after another, and measurements involving three CPCs that were all set to one specific setting, have been performed. Based on these measurements, the maximum error linked to the individual activation behavior was calculated to be at the highest at 8.1%.~~ Results of earlier studies ~~indicated a discrepancy in~~ indicate a discrepancy of the humidity dependence for sodium chloride and silver nano-particles on the detection efficiency of commerical CPCs (Sem, 2002). In the study conducted by Sem (2002), at increased RH the used CPCs had a lower cut-off diameter above 5 nm. In this size range the particle shrinkage plays an important role, ~~the~~ the ~~: The~~ already mentioned emerging liquid surface would attract further vapor molecules. Consequently, the NaCl particles can be easier activated than an insoluble seed.

However, in this study a TSI 3776 UCPC was used, which has a cut-off diameter well below 5 nm. An ~~example~~ exemplary detection efficiency measurement for the three CPC temperature settings is depicted in Figure 5. These measurements were conducted under elevated humidity conditions ($RH = 10\%$ at room temperature), which ~~leads~~ lead to a decrease of the necessary onset saturation ratio for neutral NaCl seeds as shown in Figure 3. Due to the temperature decrease in the condenser, the

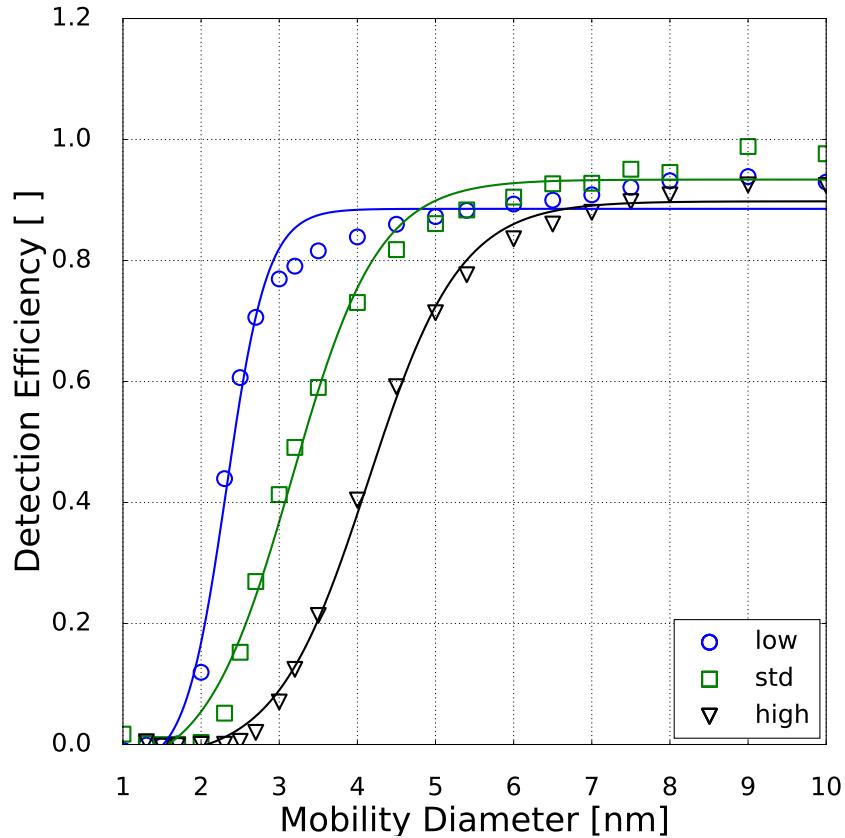


Figure 5. Detection efficiency as a function of mobility diameter for neutral sodium chloride particles. The symbols represent the measured counting efficiencies for low (circles), standard (std, squares) and high temperature (triangles) settings at 10% RH [at room temperature of the inlet line](#). The line displays a fit to the measured counting efficiencies (Wiedensohler et al., 1997). Thereby the corresponding cut-off diameter with the detection efficiency of 0.5 can be evaluated.

saturation ratio for water vapor increases up to $S = 1.6$. Studies conducted by Petersen et al. (2001) on binary heterogeneous nucleation of water-n-propanol vapor mixtures onto NaCl seeds also show that small amounts of water reduce the propanol activity substantially. Butanol is hardly miscible with water in macroscopic mixtures, but still small amounts support the nucleation. The resulting cut-off diameters for neutral, negatively and positively charged sodium chloride nano-particles are 5 shown in Figure 6. It can be clearly seen that with increasing relative humidity the cut-off diameter is decreasing for an UCPC operating at standard conditions (green) from about 3.7 to about 2.0 nm for neutral NaCl clusters. To investigate [a possible effect of](#) the charge history of neutral particles, positively and negatively charged particles were neutralized. The resulting cut-off diameters are shown in Figure 6 (left). [For sodium chloride no difference in nucleation due to](#) [Regarding](#) the charge history, [no difference in activation](#) could be found [for sodium chloride](#). Only under high n-butanol saturation [ratio-ratios \(low](#)

temperature settings) and high relative humidity conditions the previously negatively charged particles exhibit a lower cut-off diameter. In Figure 6 (right panel) the cut-off diameters as a function of RH are shown for particles of different polarity. Remarkably, for charged NaCl particles we find increased cut-off diameters compared to the neutral particles. Since the flow carrying the monodisperse aerosol monodisperse aerosols and the flow of humid air are joined together in front of the CPC 5 inlet, the increase of cut-off diameters could be a result of the increased attraction of charged NaCl particles to the water vapor under sub-saturated conditions. Thereby the Na^+ and Cl^- ions get separated and form a solvent cage around themselves (Castarède and Thomson, 2018). This solvent cage reduces the tendency of ions to aggregate (Loudon, 2009).

Li and Christopher J. Hogan (2017) performed measurements on the uptake of organic vapor molecules by nanometer scaled sodium chloride cluster ions, using a DMA coupled to a Time-of-Flight (TOF) mass spectrometer. The results show that the 10 polarity and the molecular structure of the vapor molecules control the vapor uptake. This is in agreement with our findings: The increased amount of water vapor improves the activation of sodium chloride clusters and the overall polarity of water and n-butanol vapor increases. In contrast to the SANC measurements, no significant sign preference for charge enhanced nucleation could be found. This is probably due to the cut-off diameter size which is for most of the particles > 3 nm. Except for negatively charged NaCl particles, which show a charge enhancement as it was observed with the SANC for particles 15 < 3 nm mobility diameter. In addition, the recorded cut-off diameter for high T settings is in the size range where the inverse, where the opposite temperature trend was recorded by the SANC measurements. As a result, by decreasing the temperature the needed saturation ratio to activate a NaCl particle in this size range is decreasing. Furthermore, the increasing RH supports the structural rearrangement which influences the cut-off diameter (see Figure 6). As a matter of fact, our results lead to an 20 improved detection efficiency for sodium chloride clusters. At high relative humidity and low temperature settings the detection efficiency is further promoted by charge enhanced nucleation.

Results on the cut-off diameter depending on the relative humidity at the UCPC inlet for neutralized and charged silver seeds are shown in Figure 7. For Ag particles no shrinkage in mobility diameter could be measured, and the clusters at a certain size can be assumed to be spherical (Winkler et al., 2016). As we can see in Figure 7, no relative humidity dependence on the 25 cut-off diameter within the uncertainty range was observed. However, at reduced supersaturation (black) the cut-off diameter is lower for charged Ag nanoparticles. This indicates a charge enhanced nucleation for silver aerosol particles in the measured size range. Under highly supersaturated conditions (blue) and also at standard settings (green) the charge enhanced nucleation can be neglected. Thereby the particle charge only supports the nucleation and growth process under high n-butanol and water (black) saturation vapor pressure conditions. According to the SANC measurements, no charge enhanced nucleation for 30 positively charged Ag particles could be observed. The results agree well with the SANC measurements except for positively and negatively charged Ag seeds under high T settings (see Figure 7 (right panel) right panel in Figure 7).

In general, 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 35 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 different particle solubilities are present in the atmosphere

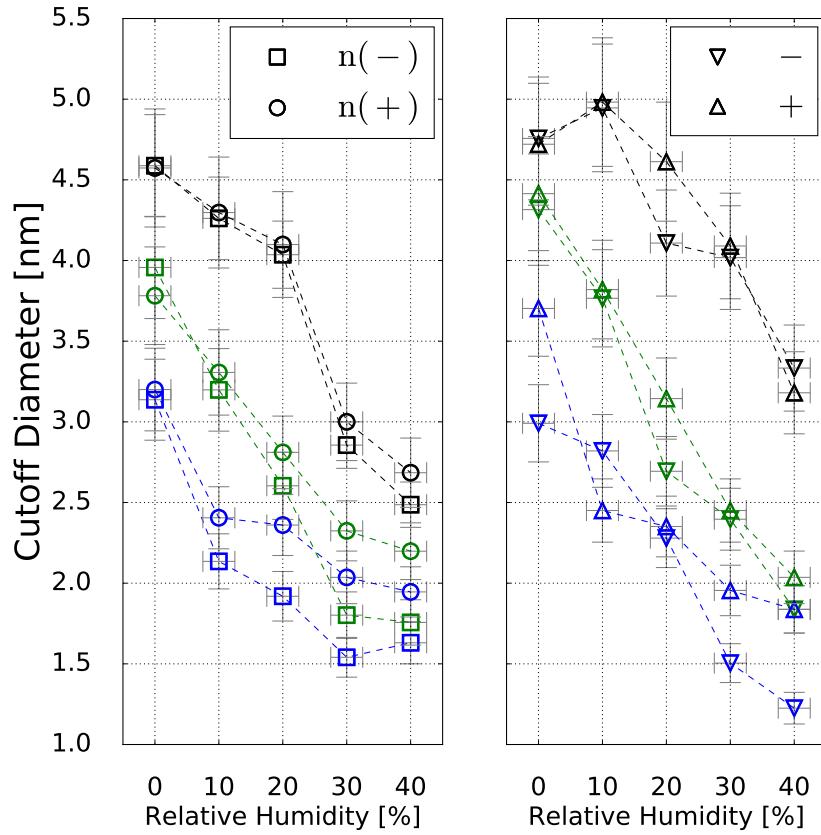


Figure 6. Cut-off diameter as a function of RH for neutral (left) and charged (right) sodium chloride seeds for low (blue), standard (green) and high (black) temperature settings.

– these uncertainties of 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 for 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.

5 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 and the source region of the seed particles can be used for data interpretation. As a result, studies that consider sea spray as a particle source
10 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.

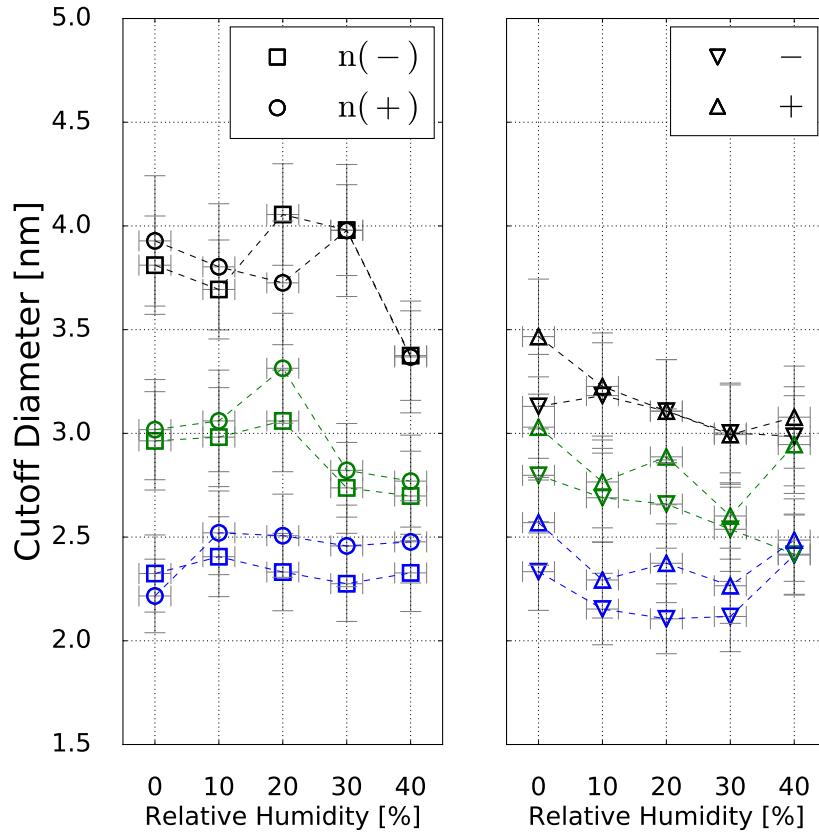


Figure 7. Cut-off diameter as a function of RH for neutral (left) and charged (right) Ag seeds for low (blue), standard (green) and high (black) temperature settings.

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. Diethylene glycol (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.

Working fluids like perfluorcarbonates (Fluorinert, FC-43) 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 Hanson et al. (2002) revealed a weak size change when using FC-43 as working fluid. In fact, the interaction between the NaCl seeds and the water molecules will be persistent if only the working fluid gets changed. To remove the influence the carrier gas should be kept dry. In case the RH cannot be kept completely dry or only dry below a certain threshold value, the effect on a change in cut-off size should be 5 considered in the data analysis. Especially at measurement sites located near the sea or at changing/high RH, which is the case for most regions.

4 Conclusions

The presented measurements conducted with expansion and continuous flow type CPCs have shown that sodium chloride particles with a mobility diameter below 10 nm indicate different activation regimes. According to the SANC measurements, 10 the required saturation ratio to activate a certain particle size is always lower for Ag particles compared to NaCl particles. This can be used as an explanation why the cut-off diameters measured for NaCl are always higher than for Ag (in butanol). Under dry conditions for particles ≤ 3 nm no inverse opposite temperature trend compared to classical Kelvin predictions was observed, however. However, for negatively charged NaCl seeds a charge enhanced activation was measured. Above 3.5 nm the charge does not play a role during the nucleation process. However, with increasing humidity We conclude that the activation 15 of NaCl particles can be enhanced -by increased humidity. For Ag this humidity dependence could not be observed, which. This is an indicator for the importance of molecular interactions between the seed and the seed and vapor molecules.

A recent recently published study on heterogeneous nucleation of n-butanol on monoatomic ions has shown that charge dependence for the critical cluster does not favor a certain polarity (Tauber et al., 2018). However, under sub-saturated conditions the charging state of the ions plays an important role during the vapor uptake. Here the NaCl particles Hence the 20 vapor molecules are in contact with the vapor molecules NaCl particles under sub-saturated conditions before the temperature drops and can already attach to the seeds. We performed measurements with NaCl seeds which are known to be hygroscopic. Therefore the water molecules dissociate the NaCl cluster and a solvation process takes place. As a result consequence, the charged sodium chloride seeds attract the vapor molecules stronger and thereby the nucleation and condensational growth can start at smaller seed sizes. In this work we assumed that the chemical composition and charging state are the driving forces of 25 nucleation and growth in the size range of the cut-off diameter of the used UCPC. Hence we recommend that in future studies the chemical composition of the generated particles in different charging states should be investigated.

As described by Li and Christopher J. Hogan (2017), the impact of vapor polarity in the measured particle size range, where interactions between single atoms are of importance, cannot be neglected. Additional water molecules increase the dipole moment of the n-butanol/water mixture and can change the structure of the sodium chloride cluster. Thereby charge effects 30 on the surface support the initial steps of nucleation which then can lead to condensational growth. As a result, the energy barrier for activating nanometer sized NaCl particles can be reduced - this is comparable to already published results for n-propanol/water mixtures conducted by Petersen et al. (2001). Our data show shows a strong effect of RH on heterogeneous nucleation of n-butanol on NaCl particles, but not for Ag seeds. This finding suggests that the different RH sensitivity is less

a consequence of binary heterogeneous nucleation, but rather attributable to changing seed properties in the interaction with vapor molecules. According to the NaCl shrinkage measurements, a change in diameter during the presence of water vapor - which we associated with a restructuring effect - could be observed.

To improve our understanding of the observed restructuring effect, future studies on heterogeneous nucleation depending 5 on different seeds and humidity should be conducted. Also the herein presented measurements could be extended with the size selection after the particle restructuring. ~~In particular the humidity~~ Additionally, higher RH conditions could be used to investigate the restructuring effect on even smaller particles. In particular, the humidity dependent activation of hygroscopic nanoparticles which are present in the atmosphere would be of great interest. Thereby, the molecular interactions between the seed and the vapor molecules can be further evaluated which may lead to a model description.

10 Our results suggest that atmospheric measurements of ambient nanoparticles should take into account possible RH effects on the instrument's cut-off diameter, when a large hygroscopic particle fraction is present. Thus, number concentration measurements should be paired with chemical and/or hygroscopicity measurements to improve the assessment of the uncertainty. If these additional measurements cannot be conducted, the location of the measurement site should be considered for data interpretation. Especially when conducting studies in marine surroundings, at which sea spray is one of the contributing particle

15 sources, special care should be taken during the data evaluation (Lawler et al., 2014; Zieger et al., 2017). As a standard procedure, in many atmospheric studies the CPC inlet flow is dried before entering the instrument. We suggest that additional monitoring of the RH of the inlet flow is critical, since the variation in RH between 0 and 40 % even shows a pronounced shift in the cut-off diameter. ~~Thereby more particles of the nucleation mode are measured. This would lead to an overestimation in the number concentration of nucleation mode particles.~~ In ambient conditions this mode usually contains high number concentrations of particles. Comparison between measurements taken in different regions with varying hygroscopic nanoparticle 20 concentrations thus need to be treated with care to avoid wrong interpretation.

Data availability. Supplementary data associated with this article can be found in the online version.

Author contributions. Christian Tauber designed the setup, Christian Tauber performed the SANC experiments, Christian Tauber, Sophia Brilke and Peter Josef Wlasits performed the detection efficiency measurements, Paulus Salomon Bauer and Gerald Köberl performed the 25 shrinkage measurements, Christian Tauber, Sophia Brilke, Peter Josef Wlasits, Gerhard Steiner and Paul Martin Winkler were involved in the scientific interpretation and discussion, and Christian Tauber, Sophia Brilke, Peter Josef Wlasits and Paul Martin Winkler wrote the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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