# Interactive comment on "Hygroscopic Properties of Aminium Sulphate Aerosols" by Grazia Rovelli et al.

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**Response to Anonymous Referee #3**

The authors would like to thank Anonymous Referee #3 for their helpful comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have to the manuscript.

***Anonymous Referee #3:*** *In this paper Grazia et al. describe the use of a Comparative Kinetic Electrodynamic Balance for investigation of the hygroscopic properties of Aminium Sulfate aerosols in comparison with water and Sodium Chloride solution drops with the same system and data collected by a number of other studies and methods. The experiments presented within are well thought out, the uncertainties in the data have been well investigated, and the results thoroughly compared with pervious data. However, I feel the tie to atmospheric chemistry, although present, is lacking. To be accepted for publication the authors should present more of a link to atmospheric processes and clearer indications of where this data this data will be most useful. Below are more detailed comments on the manuscript.*

**Response:** A similar comment was made by Referee #2 to which we have already responded. More specifically, we have added some considerable detail in the Introduction section about the different processes aminium sulphates are involved in, together with a number of references to the literature. In particular, we added more detail about the role of gaseous amines molecules in the formation of new particles. In addition, we now clearly stress the fact that nanoparticles deriving from such new particles formation events and containing aminium sulphates have the potential ability to act as cloud condensation nuclei (CCN). For this reason, investigating and quantifying precisely the hygroscopic properties of aminium sulphates is particularly atmospherically relevant, since this information is valuable in understanding of the role of such compounds in cloud activation and therefore in the indirect effects of atmospheric aerosols on climate. Please refer to the Introduction (specifically the modifications already requested by Referee #1) and to the Summary and Conclusions (section 4), which is now titled "Atmospheric Importance and Conclusions". To highlight the atmospheric relevance, we now write at the beginning of Section 4:

"Quantifying the hygroscopic properties of aminium sulphates is important for understanding and modelling of the atmospheric processes in which they are involved. In particular, the role of short-chained alkylamines in the formation of new particles has been investigated in recent literature studies and found to be significant (Section 1). Aminium sulphate-rich nanoparticles that derive from new particles formation events can potentially act as CCN, and their hygroscopic properties must be

well-characterised with the aim of reducing the overall uncertainties that currently affect our understanding of the indirect effects of atmospheric aerosols on climate. Robust and accurate data are essential for improving microphysical models of aerosol hygroscopicity; this study presents an extensive data set for an homologous series of six compounds, compared to ammonium sulphate, extending over a wide range in RH. In addition, it represents the most comprehensive characterisation of the hygroscopic response of aminium sulphate aerosol so far, complementing previous bulk phase measurements (comparable in accuracy but limited to higher water activity) and aerosol measurements at lower RH (with lower accuracy than achieved here). Previously, the bulk and aerosol measurements reported in the literature were in disagreement. Here, we report aerosol measurements that are in good agreement with the previously most accurate bulk phase data, resolving this discrepancy."

In addition, we already state later in this section the significance of these new data when compared with the earlier bulk phase data, stating:

"The main differences in approaches are that: we perform aerosol measurements that cover a wider range in water activity as compared with the bulk measurements of Sauerwein et al. (2015); and we provide direct measurement at amine-to-sulphate ratios of exactly 2:1, whereas Sauerwein et al. (2015) performed a ZSR fitting on data from solutions with variable amine-to-sulphates ratios and extrapolated water content for the exact 2:1 ratio. These new CK-EDB measurements suggest a higher level of hygroscopic growth for the aminium sulphates than previously reported by Sauerwein and co-workers when inferred from measurements over a range of amine-to-sulphates ratios; we have provided a refined parameterisation for all compositions."

***Anonymous Referee #3:*** *Page 2 line 30: Rework the sentence starting with 'Their ambient conditions...'*

**Response:** This sentence has now been reworded as follow: "The ambient concentrations of amines in the gas phase can span wide ranges, depending on the sampling location. For example, concentrations can be up to 140 mg $m^{-3}$ close to a city market (Namieśnik et al., 2003), 110-300 ng $m^{-3}$ in the exhaust gas of a waste disposal (Kallinger and Niessner, 1999), and of the order of tens of µg $m^{-3}$ inside livestock buildings (Kallinger and Niessner, 1999). Concentrations also depend on the season: for example, single amines in the gas phase at a rural site in Turkey have been reported to be in the range 0.92-7.4 ng $m^3$ in Winter and 0.29-5.16 ng $m^3$ in Summer (Akyüz, 2008)."

***Anonymous Referee #3:*** *Introduction overall: This is meant to bring everyone up to speed but I found it lacking. Consider including more information on atmospheric relevance, in situ particle formation, etc. For instance your mention of aminium sulfates role in cloud particle nucleation seems forced. If you go to the Lavi et al. paper you find right in their abstract that "Alkyl aminium sulfates have been postulated to constitute important components of nucleation and accumulation mode atmospheric aerosols." and "We infer that these species have very high CCN activity . . ."*

**Response:** We thank the referee for this suggestion. As indicated in our response to their first comment, the Introduction section has now been reworked and expanded in order to make include more information on the atmospheric relevance of the investigation of the hygroscopic properties of aminium sulphates. In particular, we state on page 3:

"The role of amines in new particles formation and growth has been highlighted by computational studies (DePalma et al., 2012; Loukonen et al., 2010; Ortega et al., 2012), as well as by laboratory (Almeida et al., 2013; Wang et al., 2010b) and field measurements (Kulmala et al., 2013; Mäkelä et al.,

2001; Smith et al., 2010). As an example, trimethylamine was found to enhance the formation and growth of new particles (Wang et al., 2010a) because of the favourable heterogeneous neutralisation reactions between the amine gaseous molecules and $H_2SO_4$-$H_2O$ clusters. Smith et al. (2010) found variable but considerable concentrations of protonated amines in nanoparticles (8-10 nm diameter) during new particles formation events (47% of detected positive ions at an urban site in Mexico, 23% at remote site in Finland and 10-35% at sampling sites in Atlanta and Boulder). Since newly formed secondary particles are estimated to contribute to 45% of cloud condensation nuclei (CCN) (Merikanto et al., 2009), the presence of amines in CCN and their hygroscopic properties need to be taken into account to improve our understanding of the indirect effects of aerosol particles on climate (McFiggans et al., 2005), a key motivator for providing refined characterisation of the hygroscopic growth of aminium salt particles in this work."

***Anonymous Referee #3:*** *Page 4 Line 6: It would be of benefit to the reader if a diagram of the EDB were included in the paper.*

**Response:** Because of the considerable length of the manuscript, and since 10 figures have already been included, we prefer not to include a diagram of the EDB instrument here; such diagrams already appear in our earlier papers. However, a schematic of the EDB setup has now been included in the supporting information and referred to in the text.

***Anonymous Referee #3:*** *Page 4 line 16: How are you controlling the RH?*

**Response:** Different RHs are obtained by mixing a wet and a dry nitrogen flow in different ratios. This information has now been included on page 4. For completeness, how the temperature is controlled in this experimental setup has also been included. These details were not included in the original version of the manuscript, instead choosing to refer the reader to previous publications (Rovelli et al., 2016; Davies et al., 2013) for a detailed description.

"The gas flow RH is modified by mixing different ratios of a humidified and a dry nitrogen flow and is inferred from the evaporation kinetics of probe droplets, as described below in this section. The temperature within the trapping chamber is controlled by a circulating a 1:1 volume mixture of water and ethylene glycol, through the lid and the bottom of the chamber."

***Anonymous Referee #3:*** *Page 4 line 22: You never explicitly state the range of RH and temperatures you are conducting your experiments at, over. Please include for completeness and link to atmospherically relevant conditions.*

**Response:** This information has now been added on page 4. Although a wide range in atmospherically relevant RHs is addressed in the measurements we present here, we have not yet performed a temperature dependence for these measurements. This will be addressed in a subsequent publication.

"Temperature and gas phase RH ranges that are accessible with this experimental setup are -25 to 50 °C and 0 to 99%, respectively. All the comparative evaporation kinetics measurements presented here were performed at 20 °C and at gas phase RH values between ~50-90%."

***Anonymous Referee #3:*** *Page 4 line 26: You mention it once (on the noted line) but I think it would help to clarify that your droplets are alternatingly injected into the system as it is possible to have multiple particles or drops trapped in an EDB simultaneously. One question I had – You're residence timescale for a single particles is less than 30 s so the RH it is exposed to is arguably constant, but to what degree does the RH change over the course of the 10+ particle runs?*

**Response:** To make sure that it is clear that all evaporation kinetics experiments are performed by alternating single probe droplets to single sample droplets, "single" (droplets) has been added at lines 15, 23, 24 (page 4) and "singly-trapped" (probe and sample droplets) has been added at line 28 (page4).

With respects to Referee #3's concerns about the stability of the gas phase RH over a run of 10+ particles, first we would like to point out that the evaporation kinetics of each sample droplet is analysed using the RH value coming from the fitting of the previous probe droplet. This ensures that even when there are very slight fluctuations in the gas phase RH, they would be taken into account in the retrieval of the hygroscopic properties of the sample droplets. That said, RH fluctuations over a typical run of 20 droplets (10 probe/10 samples) are of the order of 0.2% and never exceed 0.5% RH. In order to clarify this aspect, a few sentences have been added on page 5.

"RH fluctuations over the run of ten pairs or more of probe and sample droplets are very slight, typically of the order of 0.2% RH and never exceeding 0.5% RH. However, it should be noted that slight RH fluctuations are taken into account in our approach: the gas phase RH is monitored before every sample droplet by injecting a probe droplet and data from this probe droplet are directly used in the sample droplet evaporation analysis."

***Anonymous Referee #3:*** *Page 8 line 13: I've seen this throughout the paper: '. . . estimated by Qiu and Zhang (2012) (Qiu and Zhang, 2012) is . . .' You have essentially cited the paper twice and the second citation should be removed. Other instances can be found on page 3 line 3 and page 15 line 29. There may be others I missed.*

**Response:** Thank you for identifying this problem. The double references mentioned have now been removed and we have also checked throughout the manuscript to make sure there are no other double references remaining.

***Anonymous Referee #3:*** *Page 12 line 19: I think this is the first time you introduce ZSR, make this acronym explicit in line 16 where you introduce Zdanovskii-Stokes-Robinson expression.*

**Response:** We have added the definition of the acronym on page 12 where it is used for the first time.

***Anonymous Referee #3:*** *Page 15 line 22: Quantify fine variations.*

**Response:** 'Fine variations' at line 22, page 15, is now quantified as follows.

"Measurements from our new approach provide a level of accuracy that reveals clearly the fine variations in hygroscopic growth (down to discernible difference is $GF_r$ of order 0.01-0.02) that occur with molecular structure and substitution, and avoids the additional complexity of volatilisation of

semi-volatile components during hygroscopic growth with measurements complete in a matter of a few seconds."

***Anonymous Referee #3:*** *Page 16 last paragraph: This doesn't seem to fit. Your previous paragraph starts with 'As a final remark . . .' then this is thrown in. This goes back to my main issue of making the paper more atmospherically relevant.*

**Response:** Thank you for this comment. We agree that having "As a final remark.." at the start of the second to last paragraph is a little misleading, so we have now changed this. However, we think that the considerations in the last paragraph are quite important, because this is the first one of a series of papers where we will report measurements of the hygroscopic properties of increasingly more complex organic and mixed inorganic-inorganic aerosol systems. We have addressed the question of atmospheric relevance earlier in our response.

***Anonymous Referee #3:*** *Figure 4: You can remove legend from caption text.*

**Response:** The legend has now been removed from the caption.

***Anonymous Referee #3:*** *Figures 5 & 6: Consider labeling your subplots a-f as done in other multi-plot figures.*

**Response:** Figures 5 and 6 are now labelled with a-f to indicate each subplot. References to these labels have also been included in the main text.