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

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Response to Anonymous Referee #1

The authors would like to thank Anonymous Referee #1 for their generally positive comments on the manuscript. We respond to the specific comments made by the referee below and identify the changes we have to the manuscript.

Specific Comments:

Anonymous Referee #1: *Pg. 2 Line 32: It would be nice to give numbers for seasonal variation here since other numbers are given. Additionally, on P3 line 3 mention the location of the measurements for completeness.*

Response: Line 32 (Page 2) has now been expanded and the revised version reads as follows:

"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 site (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). Further, Pratt et al. (2009) measured a seasonal volatility dependence of alkylamines depending on the particles pH that affects the amines concentrations in the gas phase. In the condensed phase, amines can account for hundreds of pg m^{-3} or a few ng m^{-3} of aerosol mass."

The reviews by Ge at al. referenced on Line 3 (Page 3) include data for a large number of studies. Mentioning all the location of the measurements included in Ge's reviews is probably out of the scope of the overview given here. However, for clarity "at a large number of rural and urban environments" has been added (Page 3), now reading:

"An extensive review of the measured concentrations of a large number of amines both in the gas phase and in aerosols at a great variety of rural and urban environments is given by Ge et al. (2011a, 2011b)."

Anonymous Referee #1: *Pg. 3 line 5: It would be good to discuss the new particle formation in more detail with references.*

Response: We agree with Referee #1 that the role of amines in new particles formation should be discussed in more detail and therefore we added a paragraph at line 5 (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 #1: *Pg. 2 line13: Include the solubility of the amines compared to the salt products.*

Response: The solubility of both the unprotonated amines (data reworked from Ge et al. 2011b) and of five aminium sulphates (data from Clegg et al. 2013) has now been included at page 3.

"The formation of aminium sulphates and other similar aminium salts increases the solubility of short-chained alkylamines from 7-45 wt% for the unprotonated form (calculation from data in Ge et al. (2011b)) to 84-91 wt% for five aminium sulphates in Clegg et al. (2013). This, correspondingly, increases their partitioning from the gas to the condensed phase (Barsanti et al., 2009; Yli-Juuti et al., 2013)."

Anonymous Referee #1:*Pg. 4 line 23: Could you give the RHs used in this experiment here? The only place I saw them was in Figure 1 for the AS experiment.*

Response: This information has now been added at line 16, page 4.

"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 #1: *Pg. 6 line 24: What is the difference in any calculations due to less of the amine (e.g. formation of aminium bisulphate) possibly being present?*

Response: Although we have considered that the partial formation of aminium bisulphate could occur, this would increase the discrepancy that already exists between our data and that of Sauerwein et al. (2015) (for example, see Figure 7). Considerable care is taken to ensure that stoichiometric amounts of the sulphuric acid are added to the amine solution.

Anonymous Referee #1: *Pg. 8 line 5: Mention error again here in regard to the TEAS concentration measurement since you are making a direct comparison and caution that there might be error.*

Response: We agree with Anonymous Referee #1 that mentioning again the possible error on TEAS is appropriate. The following sentences have therefore been added on page 8.

"As indicated in Section 2.2, it is worth reiterating that the results presented here and below for TEAS need to be interpreted cautiously because of the uncertainty of the TEA stock solution. However, the trends that have been observed for TEAS when compared to the other five aminium sulphate systems seem to be completely plausible and this may indicate that the assumed initial TEA concentration is reasonable."

Anonymous Referee #1: *Pg. 11 line 5: It would be nice to include the trend from Saurwein 2015 somewhere in reference to the GFr and nwater/nsolute since it is not discernable from the comparison graphs in Fig. 5. Are they the same trend as your measurements?*

Response: We agree with Anonymous Referee #1 that from Figures 5 and 6 it is not possible to discern whether or not the trends observed in our work and those from Sauerwein et al. (2015) are similar. However, we already show the comparative trends from our measurements for both the methyl and ethylaminium sulphates series in Figure 3. Very similar trends are seen in the Sauerwein et al. data and we explicitly state on page 11: "However, despite the discrepancies that do exist, results from the two different experimental methods show the same qualitative hygroscopicity trends over the methyl and ethylaminium sulphates series". As a consequence, we do not feel that this merits providing an additional figure.

Anonymous Referee #1: *Pg. 13 line 15: Section 3.3 (and corresponding fig. 8) does not seem to add to the paper since the method has already been validated in a previous publication and could be moved to the supplemental information.*

Response: We thank the referee for this comment: it has suggested to us that the actual aim of this paragraph was not clearly stated and this has led to some confusion. The main aim of the assessment of reproducibility was not to provide an evaluation of the CK-EDB approach; as Anonymous Referee #1 states, this has already been reported. Instead, the aim of Section 3.3 is to report on the reproducibility of the solution preparation procedures (described in Section 2.2) to ensure that the discrepancies with the results of Sauerwein et al. (2015) are not derived from our the sample preparation. We have added a few sentences in Section 3.3 and improved the clarity of the paragraph to ensure the purpose of the section is more obvious to the reader.

"A full validation of the retrieval of the hygroscopic properties of single trapped solution droplets from CK-EDB experiments has already been presented in a previous publication (Rovelli et al. 2016), where we demonstrated the accuracy of the approach by reporting hygroscopicity measurements for well-characterised inorganic components. In this Section, we evaluate the reproducibility of the solution preparation method (Sect. 2.2) with the aim of demonstrating that the results presented in the previous Sections are not affected by any random error associated with our approach for making the sample solutions. Data obtained from three different datasets of evaporating DMAS solution droplets are compared in Fig. 8. The variation in n_{water}/n_{solute} with a_w (Panel (a)) and the change in osmotic coefficient with square root of sulphate mass fraction (Panel (b)) are calculated from three different data sets, each arising from measurements with 10 droplets and prepared from different starting stock solution of diethylaminium sulphate, obtained separately one from the other by mixing DEA and H_2SO_4

in different days. Data from Sauerwein et al. (2015) (open circles) and calculations for ammonium sulphate (E-AIM model, line) are shown for comparison. Measurements were made with droplet evaporation into a gas phase RH of ~80%. The reproducibility of the data is very satisfactory, giving further evidence that the applied solution preparation procedure coupled to the retrieval of the hygroscopic properties with CK-EDB experiments is reliable. In addition, this consistency in experimental reproducibility strongly suggests that the discrepancies with the data of Sauerwein et al. (2015) do not originate from random errors associated with the CK-EDB experiments."

Anonymous Referee #1: *Figure 1: Note in 'experimental data graph' that you alternate between the sample and a standard (or clarify when it is performed). Some additional description of a, b, c, in the figure caption would be helpful in discerning the use of the figure even though it is described well in text.*

Response: Some more detail is now given in the figure caption and a legend has been added in panel (a) in order to make clearer that sample and probe droplets are alternated.

"Figure 1: Schematics representing the retrieval of hygroscopic growth curves from comparative kinetics experiments in a CK-EDB. An experimental sequence of alternating single evaporating probe and sample droplets is collected (a). For each pair of probe and sample droplets, the gas phase RH is inferred from the evaporation kinetics of the probe (b) and this information is used to analyse the corresponding sample droplet hygroscopic properties as indicated in (c)."

Anonymous Referee #1: Figure 3: Why is there no data for MMAS and TMAS between _0.7-0.8 aw? What is the RH range used for these measurements?

Response: Measurements were taken for a large number of systems over a wide range of conditions and it became apparent only later that measurements were not available for this small range of conditions for two compounds. We concluded that the trends were sufficiently clear that additional measurements were not essential.

Anonymous Referee #1: *Fig. 3,5,6, 8, 10: In description make it explicit that the ammonium sulfate is a model that you already validated earlier in the paper (Fig. 2). On first read through I missed this and was wondering why it was compared to a model and not the experiment.*

Response: To make this clear, we have added a line in the caption of Figure 3 to explicitly say this.

"Note that only E-AIM predictions for $(NH_4)_2SO_4$ are reported in this and subsequent figures with the CK-EDB measurements and the E-AIM model compared in Figure 2."

Anonymous Referee #1: *Fig. S2: Why is the Saurwein et al. 2015 data not included here?*

Response: Data from Sauerwein et al. (2015) come from bulk water activity measurements and, hence, we do not include them in Figure S2 (GF_r vs. a_w plots). In principle, one could convert the data from Sauerwein et al. (2015) into radial growth factors, but we consider that this would not really add much to the discussion in this work.

Anonymous Referee #1: *Pg. 2 line 14: 'Because of this. . .' The 'this' is ambiguous and seemingly refers to solubility, reword sentence for clarity.*

Response: This sentence has now been reworked as follows:

"However, the physicochemical properties of aminium sulphates are much less well characterised than their inorganic counterpart, $(NH_4)_2SO_4$, even though they can play a fundamental role in the nucleation and growth of new particles (DePalma et al., 2012; Loukonen et al., 2010; Wang et al., 2010) and in cloud formation (Lavi et al., 2013)."

Anonymous Referee #1: *P6 line 15: Change the mass fraction to wt% for consistency within paper.*

Response: The mass fraction at line 15, page 6, has now been converted to weight percentage.

Anonymous Referee #1: Figures: Keep the lettering (a,b, etc.) capitalization consistent, Fig. 3 and S1 are capitalized while others are lowercase.

Response: The capitalisation of the letters in all the Figures is now uniform.

Anonymous Referee #1: *Fig. 5/6: note that the Clegg et al. 2013 data is from Qui and Zhang 2012, this was not clear.*

Response: The data plotted in Figure 5 is actually taken from Clegg et al. (2013), who reworked the radial growth factor original H-TDMA measurements from Qiu and Zhang (2012). The same is true for Figure 6, where we converted the data from Figure 5 in terms of osmotic coefficients. For the sake of clarity, we now state in the caption that the data from Clegg et al. (2013) are based on H-TDMA measurements from Qiu and Zhang (2012).

Anonymous Referee #1: *Figures 5, 6, S2, S3: Include lettering in the graphs (a,b etc.) for consistency and ease of reference in text.*

Response: Letters have now been included in the various panels in order to make references in the text clearer.