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Anonymous Referee #1

Referee's comments are in italics.

General comments

Gupta et al., present observations of the hygroscopic behaviour of $NaCl$-$MgCl_2$ *mixtures using optical microscopy, Raman microspectrometry, and scanning electron microscopy/energy dispersive X-ray spectrometry. The authors' interest in this combination of compounds stems from their potential use as surrogates for sea spray aerosol within laboratory studies. The authors are correct that existing studies of the* $NaCl$-$MgCl_2$ *are few. However, the relevance of the system studied to sea spray aerosols is limited to only one or two of the mixing ratios they studied. Despite this the manuscript represents a useful contribution to the literature so I advise its publication in ACP following minor revisions.*

Response: We thank the reviewer for the positive evaluation of our work and useful comments.

As far as the relevance of studying a wide range of mixing ratios for the $NaCl$–$MgCl_2$ system goes, several references are given in the text (Page 17800, Lines 17-27), which report chemical fractionation of nascent sea spray aerosols (SSAs) into NaCl-rich and Mg^{2+}-rich or $MgCl_2$-rich fractions during field studies and in laboratory ocean atmosphere facilities. It is evident from these studies that NaCl and $MgCl_2$ dominate the phase changes and colligative properties (including viscosity and surface tension) of nascent SSAs. Hence, the elucidation of the hygroscopic behavior and chemical microstructure of $NaCl$–$MgCl_2$ is of primary importance to explain more complex nascent SSAs in a better way. Further, the understanding of the hygroscopic behavior of a two component system is incomplete without deriving the full phase diagrams for deliquescence and efflorescence, which demands the study for a wide range of mole fractions including the eutonic composition.

As a final general comment, from the reviewers' perspective it would be useful if the authors could include some discussion on both the relevance of the offline experimental procedures used to atmospheric hydration-dehydration processes, as well as whether the 2-D area ratios that the authors present can be compared to measurements made by "online" measurements *e.g. those using Hygroscopic Tandem Differential Mobility Analyzers (HTDMAs). For example, in order to improve models which include sea spray aerosols it would be useful to convert the measured hygroscopic growth to hygroscopic growth factors (usually defined as wet divided by dry diameter assuming a spherical particle).*

Response: The conversion of the measured hygroscopic growth to hygroscopic growth factors requires the accurate values for "contact angles" vs. RH of micro-droplets and also the initial mass of solid particles (Eom et al., 2014), which is not feasible to obtain in our experimental set-up. Despite the limitation in comparing the growth factors, the experimentally measured DRH values are compared with the corresponding DRH values calculated from the thermodynamic model AIOMFAC in the deliquescence phase diagram (Figure 7). Regarding the relevance of the offline experimental procedures used to atmospheric hydration-dehydration processes, we think that the work presented here can explicitly show how this offline procedures can perform.

Specific comments

Manuscript title - In its current form the title is rather confusing. The authors refer to efflorescence during humidifying process. Presumably the authors are referring to the efflorescence they observed within one type of particle at a certain mixing ratio of NaCl-MgCl2. Given that this effect was only observed under a specific set of conditions (with a Mg^{+2} *to* Na^{+1} *ratio far higher than that of seawater) and that its inclusion makes the title confusing, I suggest the title be simplified to the following "Hygroscopic behavior of NaCl-*$MgCl_2$ *mixture particles as nascent sea-spray aerosol surrogates".*

Response: Efflorescence during humidification was observed for the first time in laboratory-generated particles. This observation is one of highlights of this work and provides a fundamental basis for understanding the hygroscopic properties of nebulized pure $MgCl_2$ and NaCl–$MgCl_2$ mixture particles more clearly.

Throughout the manuscript the authors refer to "humidifying" and "dehydration" modes. I think it is easier for the reader if they are referred to as "hydration" and "dehydration" modes.

Response: Hydration is a term also used for water (in liquid phase) absorption within salt particles. We will use the terms as “humidification” (absorption of vapor-phase water into particles/droplets) and “dehydration” (loss of aqueous-phase water from droplets) in the revised manuscript.

Page 17798 line 1 - The authors refer to the salts NaCl and $MgCl_2$ *as “the two major constituents of seawater. . . ”. This is not technically correct as any aqueous solution should be thought of as a mixture of ions and not salts. A sentence along the lines of the following would be more accurate: “Alongside* Cl^{-1}, Na^{+1} *and* SO^{-2}_4, Mg^{+2} *is a major ionic constituent of seawater. Therefore, NaCl-MgCl2 mixture particles might better represent sea-spray aerosols (SSAs) than pure NaCl.”*

Response: We thank the reviewer for pointing out this error. We will incorporate the change suggested by the reviewer in the revised manuscript.

Page 17799 line 3 - As above the authors need to be careful not to refer to salts when discussing aqueous solutions such as those of sea spray aerosol droplets. I suggest “For nascent sea spray aerosol, the major ionic constituents are Cl^{-1}, Na^{+1}, SO^{-2}_4, Mg^{+2}, Ca^{+2}, *and* K^{+1}.

Response: We will incorporate the change suggested by the reviewer in the revised manuscript.

Page 17800 line 17 - Suggest rephrase as follows “$MgCl_2$ *may play a key role in both the heterogeneous atmospheric chemistry as well as the chemical fractionation of ambient or laboratory-generated SSAs.”*

Response: Many references cited in the section support our expression. Two more references (Gaston et al., 2011; Ault et al., 2013), which also report the crucial role of $MgCl_2$ or Mg^{2+} hydrated ions in nascent SSA properties, will be added in the revised manuscript.

Page 17801 line 7 - Suggest rephrase as follows “Therefore, NaCl-$MgCl_2$ *mixture particles might better represent the hygroscopic behavior of nascent SSAs”.*

Response: Will be done as suggested.

Page 17804 line 24 - The authors state that particles larger than 0.5 μm in 2-D diameter could be analyzed using their optical microscopy setup. However, they state on Line 12 of Page 17803 that particles ranged in size between 1 and 10μm. Was it that their atomizer only produced particles larger than 1 μm or were particles smaller than this simply excluded from the analysis?

Response: The atomizer generates particles or droplets with a much larger range of size. Particles larger than 1 µm were analyzed because high quality hygroscopic OM data can be obtained from them.

Page 17805 line 5 - Although the authors state that the RH control system used for their Raman microspectrometry measurements was exactly the same as that used for the optical microscopy measurements they state a different reproducibility (±1.5% for the Raman measurements compared to ±0.5%). The authors should explain the reason for this difference.

Response: The different reproducibility was obtained by measuring DRH of pure NaCl using two different hygrometers, i.e. Testo 645 (OM, Page 17804, Line 8) and Testo 635 (RMS, Page 17805, Line 5). The RH control systems are the same for both, but RH readings are different.

Page 17895 line 23 - The authors state that they measured the chemical composition of effloresced particles but do not state what the RH was for these measurements. Given that they show that RH influences the measured particles at RH's below 10% this should be mentioned.

Response: The term, "effloresced particles" implies already solidified particles. We think there's no need to mention RH as SEM/EDX measurements are performed under vacuum.

Page 17808 line 19 - The authors do well to discuss their observations of the formation of $MgCl_2 \cdot 4H_2O$ *rather than the stable crystalline* $MgCl_2 \cdot 6H_2O$ *citing that the 2-10 minutes required for their measurements is "insufficient for the thermodynamically predicted but complex crystalline* $MgCl_2 \cdot 6H_2O$ *structure to take shape". This seems plausable. In this context it would be* *nice to know exactly the rate of change of the RH especially given the authors comments that "In real ambient conditions, the RH changes can also be abrupt." As an aside this sentence would read better as "However, it should be noted that under ambient conditions RH changes can be more abrupt."*

Response: The RH change rates of 0.3 % per 2 min. for OM and 3.0 % per 10 min. for in-situ RMS are implied from the descriptions in the experimental section: i.e., Page 17804, Line 10 and Page 17805, line 18-20. The expression will be changed as suggested.

Section 3.2.2 - The observation of three distinct types of particles for these mixing ratios is interesting although rather academic given the high Mg^{+2} *to* Na^{+1} *ratio relative to that of seawater. Given that on page 17816 line 1 the authors state ". . . the different types of particles are formed somewhat randomly. . . ". I wonder whether the authors observed any differences with particle size? Also, a number of recent studies have highlighted the importance of the particle generation method (e.g. Collins et al., 2014) when generating sea spray aerosol in the laboratory. It would be interesting to compare these atomizer results with different aerosol generation methods to see whether this affects the type of particles formed.*

Response: No size correlation was observed for different types of particles, and the different behavior was rather random due to the heterogeneous nucleation for Types B and C particles. These Types B and C as well as Type A were observed when the humidification and dehydration processes were repeated in cycles (Page 17815) and also observed in the separate in-situ RMS experiments (Page 17814, Line 20-21). Hence, the observation of three types of particles is not related to a certain atomization method. The atomizer which generated aqueous inorganic ionic droplets maintained their respective mixing ratios as in the bulk, which is vindicated by the reproducible second DRHs against the second DRHs calculated theoretically from the AIOMFAC model in the phase diagram (Figure 7). Therefore in the context of this work, it does not seem necessary to compare this system with other aerosol particle generating systems.

Page 17822 line 22 - Here the authors compare their measurements with those of Tang et al. (1997) which were measured using an electrodynamic balance (EDB). Given this comparison I miss some *discussion on how 2-D measurements such as those conducted during this study can be compared to mass based measurements of hygroscopicity such as those obtained using an EDB or electrical mobility based measurements of hygroscopicity such as those obtained using HTDMAs.*

Response: Although the growth factors cannot be convertible as stated above, DRHs, ERHs, and hygroscopic curve shapes can be compared, and the similarity between the different data is obvious as given in the text.

Page 17822 line 25 - As the authors state, seawater contains ions apart from Cl^{-1}, Na^{+1}, *and* Mg^{+2} *e.g.* SO^{-2}_4 , Ca^{+2}, *and* K^{+1}. *As such "genuine SSA" does not usually exhibit distinct MDRH or MERH which rather contradicts the authors claim of atmospheric relevance for the XNaCl = 0.9 mixture. In future work it would be useful to see these inorganic species added for comparison.*

Response: Although the dominance of NaCl and $MgCl_2$ (or Cl^-, Na^+ and Mg^{2+}) in the hygroscopic behavior of inorganic supermicron sea salt particles (or aqueous droplets) were well reported in literature (Schindelholz et al., 2014), the small different behavior of genuine SSA regarding MDRH and MERH should be investigated in the future as suggested by the reviewer.

Page 17823 line 3 - Here the authors state "These observations suggest that pure $MgCl_2$ *species (Fig. 1b) play a strong role in the hygroscopicity of the NaCl-*$MgCl_2$ *mixture system as well as the nascent ambient SSAs." I agree that differences in observed hygroscopic growth between pure NaCl particles and NaCl-*$MgCl_2$ *mixture particles suggest that* $MgCl_2$ *influences the hygroscopicity of the mixture particles. However, it does not say anything about the role of* $MgCl_2$ *in nascent sea spray particles since the authors would have had to have studied an inorganic mixture containing* SO_{-2}^{4} , Ca^{+2}, K^{+1} *etc. This sentence should be rephrased to read "These observations suggest that pure* $MgCl_2$ *species (Fig. 1b) play a strong role in the hygroscopicity of the NaCl-*$MgCl_2$ *mixture system."*

Response: $MgCl_2$ and fresh SSAs were both reported to contain water even at low RH in the references discussed in the introduction (Page 17800) unlike pure NaCl particles. These and the observation of low DRH and ERH due to the $MgCl_2{\cdot}4H_2O$-dominant eutonic component in the

NaCl-$MgCl_2$ mixture particles clearly indicate the role of $MgCl_2$ in nascent SSA hygroscopic properties as well as aqueous phase chemistry. Regarding other inorganic ions (K^+, Ca^{2+}, and SO_4^{2-}), they or their potential salts do not exhibit such low DRHs or ERHs.

Page 17823 line 6 - The language should be toned down here for the same reason as above. I suggest: "Mg^{+2}*, residing at the particle edges (core-shell type micro-structure, as shown in Fig. 9) and being in an aqueous phase even at very low RHs, i.e., at RHs higher than ~ 15.9 % and ~ 5 % in the hydration (Fig.7) and dehydration (Fig. 8) modes, respectively, may have important implications for nascent SSA heterogeneous chemistry (Wise et al., 2009; Woods et al., 2010, 2012; Liu et al., 2007)."*

Response: The "may" will be inserted as suggested.

Page 17823 line 28 - "MgCl2-rich particles can maintain. . . ". This sentence is a repeat of that on line 10 of the same page and should be removed.

Response: Will be removed.

Technical corrections

Page 17807 line 21 - Should read: ". . . typical for $MgCl_2 \cdot 4H_2O$ *(Gough et al., 2014) were observed,. . . ".*

Page 17813 line 11 - Should read: "For type B particles, three deliquescence transitions and one intermediate efflorescence transition was observed. . .

Page 17814 line 6 - Should read: "With further decreases in RH, the droplet sizes decreased noticeably at RH = 24.1-23.9 % for Type A particles (Fig. 5a), 25.1-24.9 % for Type B particles (Fig. 5b), and at RH = 24.9-23.9 for Type C particles (Fig. 5c), due to the crystallization of NaCl".

Page 17815 line 17 - Would read better as: "Efflorescence of laboratory generated particles during humidification has not been reported previously."

Page 17815 line 23 - Should read: "As shown in Fig. 6e, the Type C particle effloresced at a higher ERH of 16.8 %. . . ".

Page 17816 line 16 - As above this should read: ". . . takes place at a higher ERH range of 23.7-11.9 %. . . ".

Page 17817 line 12 - Would read better as: "For $X_{NaCl} = 0.05$ *the frequency with which particles of Type B and C are encountered is much lower (Tab. 1), most likely because the NaCl seeds were smaller. . . "*

Page 17818 line 10 - Should read: "Figures 4b and c present the. . . "

Page 17821 line 7 - Should read: "To the best of the authors' knowledge, this is the first experimental phase diagram for efflorescence of mixed NaCl-$MgCl_2$ *particles."*

Page 17822 line 4 - Should read: "Figures 9a and b show. . . ".

Page 17822 line 8 - Should read: ". . . whereas Mg and O (from $MgCl_2 \cdot 4H_2O$*) are more concentrated. . . ".*

Response: Corrections will be incorporated in the revised version. We thank the reviewer for the technical corrections.

References

Ahn, K.-H., Kim, S.-M., Jung, H.-J., Lee, M.-J., Eom, H.-J., Maskey, S., and Ro, C.-U.: Combined Use of Optical and Electron Microscopic Techniques for the Measurement of Hygroscopic Property, Chemical Composition, and Morphology of Individual Aerosol Particles†, Anal. Chem., 82, 7999-8009, 10.1021/ac101432y, 2010.

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Schindelholz, E., Risteen, B. E., and Kelly, R. G.: Effect of Relative Humidity on Corrosion of Steel under Sea Salt Aerosol Proxies: II. MgCl2, Artificial Seawater, J. Electrochem. Soc., 161, C460-C470, 10.1149/2.0231410jes, 2014.