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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evolution of particle composition in CLOUD nucleation experiments" *by* H. Keskinen et al.

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REFEREE 1: Review of "Evolution of particle composition in CLOUD nucleation experiments" by Keskinen et al. This paper estimates the evolution of particle composition during the growth of particles from diameters of _1-2 nm to diameters larger than 50 nm. The paper uses a combination of instruments to estimate the organic vs. inorganic fraction across this complete size range. I feel that the paper is lacking a discussion (and possibly a very useful analysis) of *why* the inorganic to organic composition changes with size. Once this and other (more minor) comments have been addressed, I recommend this paper be publishedin ACP. General comment There was no discussion in the paper regarding why the organic composition increases during growth. Pierce et al. (2011) and Donahue et al. (2011) estimated that this occurs because of small particles reaching equilibrium with the vapor phase more quickly than larger particles, and only the lowest volatility organics can condense onto the smallest particles. However, in your experiments, there is the confounding factor that the gas-phase production of sulfuric acid and low-volatility organics may be occuring at different rates. If the sulfuric acid is being formed more rapidly than the low-volatily organics, this may also cause the particles to increase in organic composition later, as they grow. Please add a discussion of these possibilities. In my opinion, the usefulness of the paper could increase greatly if additional analysis were done to quantify why/how the organic composition increases during growth. The relative sulfuric acid vs. organic aerosol formation rates could be determined from looking at the bulk mass from the AMS and the concentrations of the precursors (if they are monitored). If the oxidative timescale of both the precursors is similar or both smaller than the growth timescale, then the change in composition with growth is likely due to only the lowest-volatility organics condensing to the small particles with higher volatilities being able to condense as the particles grow. It should be possible to estimate a volatility distribution based on the change in organic fraction with time. However, one thing that might make this estimate tricky is that multi-generational organic chemistry will be causing the organic volatility distribution to evolve even as the particles grow. Either way, please consider this analysis. Co-authors Riipinen and Donahue should have good thoughts on this. Pierce, J.R., Riipinen, I., Kulmala, M., Ehn, Petaja, T., Junninen, H., Worsnop, D.R., Donahue, N.M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, Atmospheric Chemistry and Physics, 11, 9019-9036, doi:10.5194/acp-11-9019-2011, 2011. Donahue, N.M., Trump, E.R., Pierce, J.R., Riipinen, I.: Theoretical Constraints on Pure Vapor-Pressure Driven Condensation of Organics to Ultrafine Particles, Geophysical Research Letters , 38, L16801, doi:10.1029/2011GL048115, 2011.

– We thank the reviewer for bringing up the important point of discussing the reasons behind the increasing organic fraction. There are indeed essentially two possible explanations: 1) The Kelvin effect inhibits the condensation of all organic condensable

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molecules at the smallest sizes; 2) The gas phase concentrations of sulphuric acid and condensable organics have different time scales. Since (in our case) the precursors of both sulphate and condensable organics are produced primarily via reactions with OH, and the temporal profiles of the precursors are similar (although PD concentration rises slightly before SO2, see Fig. X), we think that in our case the former explanation is more likely. However, without knowing the exact chemical pathways producing the condensable organic, it is difficult to draw a definite conclusion about this. While a detailed analysis of the volatility distributions of the organic vapours would definitely be interesting, we feel that it is out of the scope of this paper and deserves a study of its own. We have added a brief discussion on these possible reasons for the increasing organic fraction in the particles to the revised manuscript.

Added to the introduction:

“It is possible to gain information on the nucleated nanoparticles’ size-dependent composition during their growth via the direct and indirect experimental methods presented above. This can provide information on the topical question of the organic contribution to particle growth during nucleation (Pierce et al. (2011) and Donahue et al. (2011), Riipinen et al., 2012). ”

Added to the results:

“Overall, the size dependent composition analysis made here provides valuable information about the sulfate and organic contribution to nanoparticle growth. According to our analysis, the particles consists mostly of SA right after nucleation, but the inorganic fraction gradually decreases with particle growth (Fig. 5 c), while the organic fraction increases (Fig 5 a). There are two possible explanations: 1) The Kelvin effect inhibits the condensation of all organic condensable molecules at the smallest sizes; 2) The gas phase concentrations of sulphuric acid and condensable organics have different time scales (Pierce et al. (2011) and Donahue et al. (2011)). As the precursors of both sulphate and condensable organics are produced primarily via reactions with OH, and

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the temporal profiles of the precursors in the chamber are similar (Table 1), in our case the former explanation is more likely. However, without knowing the exact chemical pathways which produce the condensable organic, it is difficult to be certain about this. “

Specific comments P31073 L20-22: Why are different size ranges given (e.g. 2-63 nm vs. 2-50 nm)? And when you say “sulfuric acid” volume fraction, I think you mean “sulfate” or “inorganic”. I didn’t see any evidence in the paper that the aerosols were very acidic (i.e. unneutralized sulfuric acid) at 2 nm (though this may be related to a mis-understanding that I have in a later comment).

–The organic fraction was determined for the size range from 2-63 nm from Api-TOF (2 nm), HTDMA (15-50 nm), CCNC (40-63 nm) and AMS (65 nm) measurements. The sulphuric acid fraction was determined from Api-TOF (2 nm), HTDMA/OTDMA (15-50 nm) measurements and thus size range ends to the 50 nm. We did mean sulphuric acid; see equation (9).

P31074 L15-18: This is not totally accurate. The sentence makes it seem as if we call the entire particle an “SOA particle” when SOA condenses onto the particle (even if the particle is not entirely SOA).

–Sentence replaced by:

“Particles are referred to as secondary organic aerosol (SOA) when oxidation products of volatile organic compounds (VOCs), emitted by biogenic and anthropogenic sources, participate in the formation and growth process of these newly formed atmospheric particles (Laaksonen et al., 2008; Kanakidou et al., 2005; Jimenez et al., 2009; Claeys et al., 2004; Hallquist et al., 2009).”

P31074 L21: Why is “state-of-the-art” italicized?

–Italics removed.

Introduction: The intro focuses largely on the hygroscopic growth of particles, but it

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doesn't discuss much about the growth of nucleated particles (by inorganics vs. organics). The contributors to aerosol growth appear to be on of the main focuses of the results, so they should be motivated in the introduction.

–Introduction updated. See 1st answer "Added to the Introduction".

P31076 L20-23: Please give a few more details on the GR analysis here. I believe this is where you calculate the maximum growth rate due to H2SO4 vapours (measured from the CIMS) alone and compare this to the actual growth rate. This gives an estimate of the amount of sulfuric acid condensing vs. the amount of organics condensing.

–Yes. Details added. Text in manuscript:

"GRs were also used to obtain the volume fraction of sulphuric acid in nucleated nanoparticles. In the GR analysis, we used the SA gas phase concentration measured by the CIMS. The theoretical maximum GR from condensation of gas phase SA onto the particles was calculated according to the method of Nieminen et al., 2010. The ratio of GR from SA condensation to the observed particle GR calculated based on SMPS data gives the fraction of particle growth explained by sulphuric acid."

P31077 L1-2 and P31079 L17: The size ranges for CCNC measurements differ.

–The right size range was 43-125 nm. This has been corrected in manuscript.

P31083 L14: Measured organic fraction from which instruments?

–This sentence has been replaced with, "The organic fraction was derived from hygroscopicity measurements made with the HTDMA."

P31083 L21-24: Diffusivity/molar mass is not the only (or necessarily the primary) driver for the timescale of reaching equillibrium. Higher volatility species reach equilibrium faster because condensation/evaporate occurs more rapidly to drive towards equillibrium. –We agree with the referee and we have modified the text: "This approach includes the assumption that ammonia, DMA and water, due to their higher gas phase concentrations, smaller molar masses, or shorter diffusion time scales, diffuse fast enough to maintain gas-liquid equilibrium while sulphuric acid and organic compounds condense on the particle."

P31084 L17: "10 : 10", please make "10:10". This confused me for a bit. Discussion of Fig. 1B: Approximately how many sulfuric acid molecules are in a 1.2 nm cluster. This would be a useful reference to have.

–Changed 10 : 10 to 10:10. There were four SA molecules in that cluster. Information added to the manuscript:

"Here we present the measurements with sulphuric acid and ammonia in the CLOUD chamber (Run A, Table 1). The gas concentrations measured in the chamber are shown in Table 1. Here the UVS was turned on at 10:10, which immediately caused nucleation and high particle growth rates (Fig. 1a). At the start of the nucleation, we can see from the APi-TOF measurements (Fig. 1b) that initially there were pure SA clusters below the size of 1.2 nm with four SA molecules. At larger cluster sizes from 1.2 to 1.9 nm (4-19 molecules), a fraction of the SA was associated with NH3."

Section 3.2.1: Why are API-TOF results not shown for this run?

–The API-TOF results have been included:

"In this section, we present the TDMA and CCNC results for particles formed in the presence of sulphuric acid, ammonia and organics (oxidation products of PD) with strong UV light (run B in Table 1). At the beginning of the experiment, the high intensity UV light source was turned on. The nucleated clusters ($\sim$2 nm) had a high organic mass fraction of 75 $\pm$ 10 % right after the UV was switched on, based on measurements from the API-TOF. This experiment resulted in fast growth (GR = 84nmh$-$1 for mobility diameters of 47 to 80 nm) of the nucleated particles (Fig. 2a). "

P31086 L14: Need comma between CCNC and O-TDMA.

–Comma added.

Figure 3 and P31086 L13: “runs C-G”. Figure 3 only shows 1 run, right (or maybe 2)? How could this be runs C-G? I guess I can kinda pick out 5 separate bananas (3 of the 5 are faint). Please make your definition of a “run” clear in the text. I was thinking that a “run” was a full experiment, but maybe each run is the injection of precursors, which could happen many times during a single experiment?

–Yes, really good point as the experiment plotted in Figure 3 included several runs referring the CLOUD experiment run number. However, our results presented in the paper were specified from the certain run with “stable” gas phase conditions. The marking and way we show the results was not clear. Clarification has been added to the text and to Fig. 3. The banana which our measurement followed has been marked with arrow now in Fig. 3. Our measurements were made under the conditions in Exp E in the previous table, now marked Run C. Updated text in manuscript:

“In Fig. 3, the evolution of the measured number size distributions during the experiment including several nucleation events is shown. The studied particle nucleation event (Figure 3, Table 1, Run C) has a growth rate of GR = 3.24nmh−1 for particles with mobility diameter of 26–40 nm, and GR = 3.8nmh−1 for particles with mobility diameter of 41–60 nm. The TDMA and CCNC results presented here were measured during the intensive growth period (15–30 nm) and under more stable conditions (50–80 nm). The measurements reported here were carried out during run C, which has been marked with an arrow in Fig. 3 (Table 1, Run C).”

P31088 L1: Why “(Fig. 1)” here? I was confused and trying to look in Figure 1 for where you might be extrapolating some value from it (but you aren’t extrapolating anything from it, right?). Best to remove “(Fig. 1)”, I think.

–(Fig. 1) Removed.

P31089 L18-end-of-paragraph and Figure 5c: When you say “SA”, do you mean un-neatralized sulfuric acid, or do you mean “sulfate” or “inorganics”? I was assuming that you meant un-neutralized sulfuric acid, but then I was confused when I read the sentence starting at L25 that only mentions AS and AbS, not SA. If it is un-neutralized sulfuric acid, it is very acidic, and you should mention this.

–Yes, we meant un-neutralized. Clarified in the text: "Next we use the derived organic fraction shown in Fig. 5b to estimate the distribution of un-neutralized SA in the particles by following the procedure described in Sect. 2.4 (Eq. 8). …. It is important to note that the simple experimental approach (Eq. 9) used to analyse the composition is not comprehensive as it only includes oxidized organics, SA, AS and AbS. In fact, aminium salts are also likely to be present even with very low concentrations (Table 1)."

REFEREE 2

This study reports on chemical and hygroscopicity measurements from CLOUD nucleation experiments involving both inorganic and organic species. A major result is that the organic fraction of the particles increased as particle diameters increased from _2 nm up to over 50 nm in diameter. The experiments and measurements are of high quality. Numerous instruments were used to carry out the measurements and that data are reported in a concise manner. The manuscript is written well, and the only issue evident in the presentation is that some of the figures are very difficult to see. The topic will be of great interest to ACP. I support publication of this work after the authors go into detail as to why the organic fraction increases with size/growth. Currently the reader is just told that this result was observed and is left to try to piece together on their own as to why this is. The authors can strengthen their paper by providing reasons for this key finding in a convincing way other than simply speculating in a few sentences (i.e. do some calculations and additional work).

–The figures quality has been improved. Also we agree with the referee and have provided more details about the particle growth vs organic fraction. "Added to the results"

"Overall, the size dependent composition analysis made here provides valuable information about the sulfate and organic contribution to nanoparticle growth. According to our analysis, the particles consists mostly of SA right after nucleation, but the inorganic fraction gradually decreases with particle growth (Fig. 5 c), while the organic fraction increases (Fig 5 a). There are two possible explanations: 1) The Kelvin effect inhibits the condensation of all organic condensable molecules at the smallest sizes; 2) The gas phase concentrations of sulphuric acid and condensable organics have different time scales (Pierce et al. (2011) and Donahue et al. (2011)). As the precursors of both sulphate and condensable organics are produced primarily via reactions with OH, and the temporal profiles of the precursors in the chamber are similar (Table 1), in our case the former explanation is more likely. However, without knowing the exact chemical pathways which produce the condensable organic, it is difficult to be certain about this.

Minor comments: Figure 5c: y-axis label is spelled wrong. Also, many other y-axis labels appear to have an overlap issue where some text covers other text. General comment about Figures: it is very hard to see panels b-d in Figure 1; text size and marker sizes can be bigger in many of the figures to make it easier for readers to follow what is trying to be shown.

–All Figs improved and mistakes corrected. See supplement.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C13919/2013/acpd-12-C13919-2013-supplement.zip

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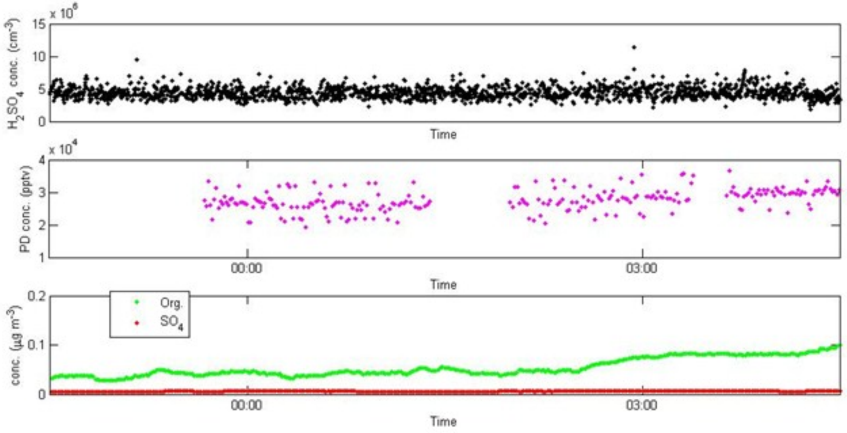

Fig. 1. Figure X. The time evolution of gas phase precursor (SA, PD) concentrations and particle phase (Dp > 50 nm) composition.

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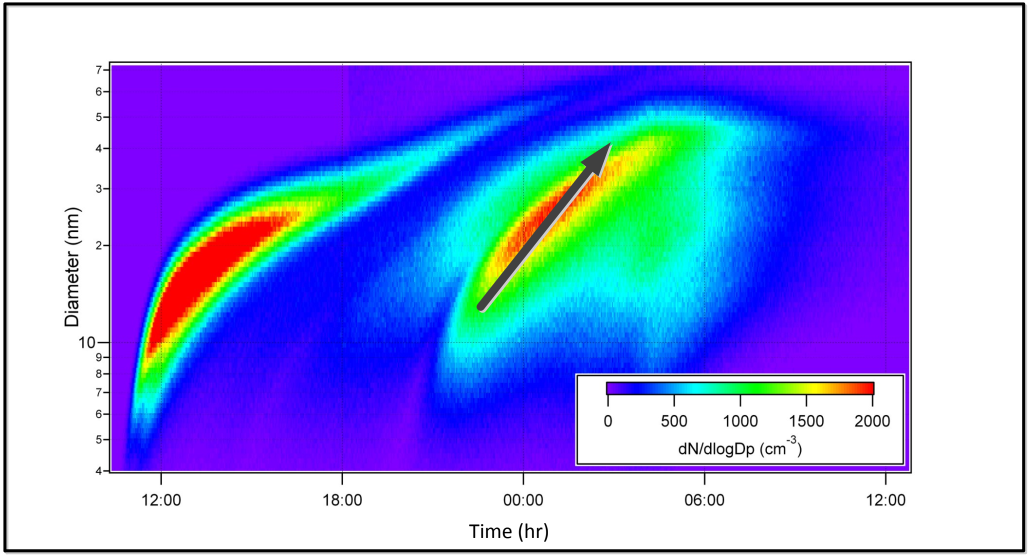

Fig. 2. Fig. 3. The evolution of the particle size distribution in the presence of sulphuric acid, ammonia, dimethylamine and pinanediol in the CLOUD chamber. The event studied in detail (Run C, Table 1) is m

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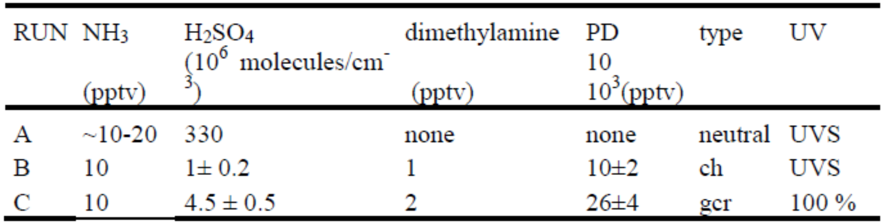

RUN	NH_3 (pptv)	H_2SO_4 (10^6 molecules/cm^{-3})	dimethylamine (pptv)	PD 10 10^3(pptv)	type	UV
A	~10-20	330	none	none	neutral	UVS
B	10	1± 0.2	1	10±2	ch	UVS
C	10	4.5 ± 0.5	2	26±4	gcr	100 %

Fig. 3. Updated Table 1