

## Authors Response

The authors have compiled the responses as follows. Reviews are in **Bold**. Author responses are numbered with [A0, A1, A2 ...]. Line numbers in the responses are consistent with those in the reviews.

### **Anonymous Referee #1**

**Received and published: 20 February 2014**

**The manuscript presents results from chamber experiments where the hygroscopicity of particles formed from amine oxidation products is studied. Lately the role of amines in the formation of SOA has been acknowledged and here new results are presented on the hygroscopicity of these products. Also important is the increasing knowledge of the semivolatile SOA and how they are affecting the CCN measurements. Thus the topic is important and of interest for ACP readers. I have only few comments, and after addressing them I recommend the manuscript to be published in ACP.**

### **Specific comments**

**Abstract: Abstract is quite long and heavy to follow with lot of results. It could be improved by emphasizing more the main findings and leaving out some less important details.**

[A0] The abstract is revised per reviewer's comment, leaving out less important detail results.

Aliphatic amines can form secondary aerosol via oxidation with atmospheric radicals (e.g. hydroxyl radical and nitrate radical). The particle composition can contain both secondary organic aerosol (SOA) and inorganic salts. The fraction of organic to inorganic materials in the particulate phase influences aerosol hygroscopicity and cloud condensation nuclei (CCN) activity. SOA formed from trimethylamine (TMA) and butylamine (BA) reactions with hydroxyl radical (OH) is composed of organic material of low hygroscopicity (single hygroscopicity parameter,  $\kappa \leq 0.25$ ). Secondary aerosol formed from the tertiary aliphatic amine (TMA) with  $N_2O_5$  (source of nitrate radical,  $NO_3$ ), contains less volatile compounds than the primary aliphatic amine (BA) aerosol. As RH increases, inorganic amine salts are formed as a result of acid-base reactions. The CCN activity of the humid TMA- $N_2O_5$  aerosol obeys Zdanovskii, Stokes, and Robinson (ZSR) ideal mixing rules. The humid BA+ $N_2O_5$  aerosol products were found to be very sensitive to the temperature at which the measurements were made within the stream-wise continuous flow thermal gradient CCN counter;  $\kappa$  ranges from 0.4 to 0.7 dependent on the instrument supersaturation ( $ss$ ) settings. The variance of the measured aerosol  $\kappa$  values indicates that simple ZSR rules cannot be applied to the CCN results from the primary aliphatic amine system. Overall, aliphatic amine aerosol systems  $\kappa$  ranges from  $0.2 < \kappa < 0.7$ . This work indicates that aerosols formed via nighttime reactions with amines are likely to produce hygroscopic and volatile aerosol whereas photochemical reactions with OH produce secondary organic aerosol of lower CCN activity. The contributions of semi-volatile secondary organic and inorganic material from aliphatic amines must be considered for accurate hygroscopicity and CCN predictions from aliphatic amine systems.

**Abstract: “The aerosol behaves non-ideally, hence simple ZSR rules cannot be applied to the CCN results from the primary aliphatic amine system”. What you mean by non-ideal aerosol? If aerosol is semivolatile it does not make it non ideal, and it is more measurement issue that ZSR is not working.**

[A1] Change to “The variance of the measured aerosol  $\kappa$  values indicates that simple ZSR rules cannot be applied to the CCN results from the primary aliphatic amine system.”

**In the introduction the atmospheric relevance of amines is only shortly mentioned without really discussing how important they are. How big fraction of all organics is made of amines? How are they distributed in the atmosphere and what are the sources?**

[A2] The sources of amines in the atmosphere has been comprehensively reviewed in Ge et al., 2011, so we did not repeat in this paper. However, we agree that the brief introduction of the atmospheric relevance of amine should be included.

Added to the introduction “Due to the common impression of most low-molecular weight amines being highly volatile, little attention has been devoted to the gas/particle phase partitioning of amine-containing aerosol. Source of aliphatic amines includes combustion, biomass burning, agricultural practices (e.g. vegetation, animal husbandry) and the ocean (reviewed in Ge et al., 2010a). The ambient concentration of amine can be as much as 14-23% of that of ammonia even in the presence of ammonia (Sorooshian et al., 2008). “

**Page 35, line 16: How atmospherically relevant are the measurements conducted at RH less than 0.1%?**

[A3] Measurements conducted at  $RH < 0.1\%$  provide information for chemical reactions without the involvement of water vapor, which is indispensable for understanding the atmospheric behavior of amines.

**Methods: The precursor concentrations used in the experiments are quite high. Could it be that semivolatiles already evaporate when they are classified in the DMA and this could affect the results?**

[A4] The composition of semivolatile organic aerosol in the DMA is the same as in the reaction chamber as they are both housed in the same enclosure. Thus there is no evaporation in the DMA.

**Page 41: How is ammonia formed?**

[A5] This is a great question. The instrumentation used in this study cannot provide that answer. However it is the subject of work which will be explored in further detail in a future submission.

**Page 42: “Therefore, there are likely differences in the aerosol solute composition measured at high and low ss.” What if there are just differences in the aerosol evaporation rate or even morphology?**

[A6] Here we assume the reviewer is referring to the difference of evaporation rate and morphology during the CCN activity measurement. It is possible that evaporation rate is different and it also results in different “aerosol solute composition”. As for morphology, we do not believe it varies much at  $ss$  0.2-0.9%.

**Page 42: Only the top and bottom temperatures are presented for CCN-column. It would be also interesting to know how high the temperature was before particles are activated to cloud droplets. I assume that drops will not evaporate after the activation if supersaturation is maintained in the chamber. Is the position of maximum supersaturation dependent on the flow and temperature gradient in the DMT CCN column? What is the relative humidity of sample air arriving into the CCN column and what is the relative humidity that sample experiences as a function of time? Now it is difficult to make a connection between results in Figures 3 and 4.**

[A7] The temperature and relative humidity of particles entering the CCN column is the same as the reaction chamber, around 26 °C and ~30% (for humid BA-N<sub>2</sub>O<sub>5</sub> reaction). In a normally functioning DMT CCN counter, the maximum supersaturation is reached in the first half of the column to ensure CCN activation and enough time for droplet growth, and is dependent on flow rate and temperature gradient. We are not sure about the time profile of relative humidity that aerosol sample experienced, but the activation occurs a few seconds after the sample enters the CCN column and will vary slightly for less and more hygroscopic materials. Additional information on the temperature and RH profiles in the instrument can be found in Roberts and Nenes, 2005.

Both Figure 3 and 4 plot measured  $\kappa$  values for aerosol formed in the humid BA-N<sub>2</sub>O<sub>5</sub> reaction. Figure 3 is time series of  $\kappa$  measured at various *ss*, while Figure 4 plots  $\kappa$  from measurement at *ss*~0.37% which is reached by varying temperature gradient and flow rate. We have clarified this in the text.

**Table 1: What is the hygroscopicity of ammonium nitrate based on your experiments (on Page 43, line 7)? Do you see evaporation of nitrate and ammonia?**

[A8] Based on the calibration of *ss* using ammonium sulfate, the hygroscopicity parameter of ammonium nitrate is 0.74 (consistent with theoretical values). We did not see evaporation of nitrate and ammonia.

**Table 1: There is a big difference between TMA HNO<sub>3</sub> and BA HNO<sub>3</sub> hygroscopicities (0.72 and 0.52). What is causing that? Compared to ammonium nitrate the hygroscopicity of TMA HNO<sub>3</sub> seems to be quite high.**

[A9] The trimethylammonium nitrate salt is 2-3 times more soluble than ammonium nitrate, two orders of magnitude more volatile (comparing solid/gas equilibrium dissociation constant, Table 5, Ge et al., 2011a), suggesting higher hygroscopicity. Little is known about the thermodynamic properties about BA·HNO<sub>3</sub>, however, inferring from butylamine chloride salt, it may have lower solubility and volatility than ammonium nitrate and trimethylammonium nitrate.

**Anonymous Referee #2**

**Received and published: 18 February 2014**

**General comments**

**Tang et al. have measured CCN activity ( $\kappa$ ) and volatility of aliphatic amine secondary aerosol. Their results show that aerosol hygroscopicity and volatility depend on the amine precursor, oxidation method and humidity. One of the studied amine aerosols is so volatile that particles evaporate in a thermal gradient CCN counter, which has an effect on the observed CCN activity.**

**Although there are several studies about the formation and composition of amine secondary aerosol, there are only a few studies about their CCN activity and volatility. The findings of Tang et al. are interesting and the topic of the paper is within the scope of ACP. The paper is compact, well-**

written and clear. Therefore, I recommend this paper for publication after a few corrections and clarifications.

#### Specific comments

- 1) **Page 37, lines 19-20: Typically  $T_1$  is higher than the sample temperature, and the temperature set points change automatically with the sample temperature while keeping a constant  $\Delta T$ ; was this the case in these experiments? If yes, please clarify this part of the text. How constant was  $T_1$  and what was the difference between  $T_1$  and the temperature of the reactor chamber? Could the observed changes in  $T_1$  or in the temperature difference between the CCN counter and the reactor chamber have an effect on the conclusions about volatility?**

[A10] The temperature difference  $\Delta T$  is constant for each  $ss$  setting, while  $T_1$  (temperature at the top of the CCN counter column) is very close to the sample temperature (i.e. the reactor chamber temperature). Both the reactor chamber and the CCN counter are inside a temperature-stabilized building. The ambient temperature in the building is maintained at  $26 \pm 1$  °C, and we did not observe a temperature difference between  $T_1$  and the reactor temperature larger than 2 °C. Thus, we can exclude the possibility of temperature difference between CCN counter and reactor chamber affecting our conclusion about volatility.

**Related to the previous comment, could the conclusions on CCN activity depend on the location of the maximum supersaturation, which also gives the temperature where the particles activate? Theoretically (e.g. Lance et al., Mapping the Operation of the DMT Continuous Flow CCN Counter, Aerosol Sci. Tech., 40, 242-254, 2006), increasing flow rate means that the maximum center line supersaturation is reached earlier in the CCN column. It is mentioned in the paper (page 42, lines 17-18) that the total residence time increases with decreasing flow rate, but at the same time particles activate earlier and in the cooler part of the column, which could actually decrease the evaporation.**

[A11] It is reasonable to infer that the high  $\Delta T$ , low flow rate and long retention time altogether result in the evaporation. However, when flow rate and retention time was not changed, at high  $ss$  we observed the abnormally high  $\kappa$  value measured by CCN counter. Since activation normally occurs in the first half of the CCN column and droplets do not evaporate after formation and thus the location of maximum supersaturation does not matter.

- 2) **The VTDMA measurements showed that especially the humid butylamine- $N_2O_5$  secondary aerosol is highly volatile, but this doesn't seem to cause problems in the CCN measurements when the column temperature difference is smaller than 21 °C, why? Volatile material could be evaporated already before the aerosol reaches the CCN counter and also in the CCN counter, and either one these would change the observed CCN activity. If there are indications that particles are evaporating, this should be mentioned as an uncertainty for calculated  $\kappa$  values especially for the particles composed of volatile amines.**

[A12] Before aerosol reaches the CCN counter, it already equilibrates between gas and particle phase. Once entering the CCN column, the aerosol is immediately surrounded by water vapor at supersaturated relative humidity, so it is different from being exposed to charcoal in the VTDMA. There is little indication that particles will evaporate before reaching instrumentation. The following comment and response address why.

**The observed step-like change in the CCN activity (Fig. 4 and page 42, line 19) when the column temperature difference changes just 7 °C is interesting; does it mean that the evaporation starts only after a certain minimum temperature and/or residence time?**

[A13] Yes, our findings suggest that the evaporation only affects the measurement when the temperature gradient/ retention time within the CCN counter column exceeds a certain value as reported in our work.

**Was the CCN/CN ratio approaching unity when the chamber temperature difference was smaller than 21 °C or for other compounds at 21 °C? If not, could this cause problems for the SMCA data analysis (e.g. multiply charged particles could become important)?**

[A14] The CCN/CN ratio was about unity for all reported measurements. So it did not cause any issues for the SMCA analysis.

**3) Especially approximate VFR (Volume Fraction Remaining) values from Fig. 1 and possibly also salt mass fractions could be added to Table 1. This would make it easier to see the similarities and differences between the experiments.**

[A15] The VFR values and the corresponding VTDMA temperature have been added to Table 1.

Amine	Oxidant	RH (%)	$\kappa$	VTDMA Temp (°C)	VFR
TMA	H <sub>2</sub> O <sub>2</sub>	<0.1	0.18±0.02	100	0.75±0.02*
		30			
	N <sub>2</sub> O <sub>5</sub>	<0.1	0.20±0.02	100	0.7±0.02*
		~25	0.28±0.02	100	0.38±0.02*
BA	H <sub>2</sub> O <sub>2</sub>	<0.1	0.23±0.01	50	0.21-0.91
		~37	0.25±0.03	50	0.16-0.38
	N <sub>2</sub> O <sub>5</sub>	<0.1	0.19±0.04	50	0.22-0.48
		12	0.48±0.10	50	0.07-0.35
	N <sub>2</sub> O <sub>5</sub>	23	0.33±0.08	50	0.06-0.14
		30	0.49±0.08		
		35	0.60±0.10	35	0.03±0.01*
			0.72±0.04		
			0.53±0.03	35	0.10±0.06
			0.74		

\*Average ± standard deviation

## **Technical corrections**

**Page 32, line 3: Delete word "composition"**

**Page 32, line 4: Maybe "The ratio of organic to inorganic..." or "The fraction of organic materials..."**

**Page 34, lines 4-6: Maybe "...as well as in the..."? Could use insoluble instead of nonsoluble and variability (or similar term) instead of variance, which refers to statistics.**

**Page 34, line 20: Maybe "ambient aerosol"?**

**Page 37, line 5: Does this inversion procedure account for multiply charged particles or maybe something else? Is this the SMCA or SMPS inversion method? Please clarify.**

**Page 38, line 14: I guess  $S_c$  is the critical saturation ratio?**

**Page 40, line 17: The 30 % should refer to percentage points; a change from 30 % to 60 % means doubling of the evaporated volume.**

**Page 42, line 4: Could use variability (or similar term) instead of standard deviation, which refers to statistics.**

**Page 43, line 21: Could replace variance by e.g. variability.**

**Page 45, reference Finlayson-Pitts and Pitts: Check the information.**

[A16] All technical corrections have been made.