acp-2016-835

Reply to Reviewer #1

This reply is formatted as follows:

Reviewer's comments

> Authors' reply
>
> Changes to Text

The study reports on a valuable dataset collected at the Schmucke mountain site in central Germany in September and October 2010. They collected aerosol composition data using a C-ToF-AMS downstream of a CVI inlet, which selectively samples droplets and rejects interstitial aerosol particles. The topic of the paper is of importance and of interest to readers of this journal. In general, measurements of this nature are difficult to make, especially at mountain sites, and thus the data are of importance to document in the literature. The analysis by the authors leads to a few interesting conclusions:
(i) a significant fraction of submicron aerosol partitioned to the cloud liquid phase (85% on average); (ii) nitrate generally exhibited higher scavenging efficiencies as compared to ammonium, sulfate, and organics (black carbon was the lowest); (iii) nitrate and ammonium mass fractions were enhanced in droplet residual particles, with a speculation made about temperature playing a role in this finding; (iv) the oxidation state of organic matter in droplet residuals was also shown to have a potential temperature dependence. I found the analysis to be supportive of the conclusions reached. The figures can benefit in some parts from better aesthetic quality, including larger font size. Figure 3 in particular could use improvement. The title of the work is supportive of the contents of the paper. I recommend publication of this work after the authors address my suggested minor revisions below. Most of the specific comments relate to incorporating the work of others that may have gone overlooked but are highly relevant to the discussion topics of this paper.

> We thank the reviewer for this positive rating of our manuscript

Specific Comments: Page 2, Line 33-36: Other papers have also shown this that should be mentioned: Asa-Awuku et al. (2015). CCN properties of organic aerosol collected below and within marine stratocumulus clouds near Monterey California, Atmosphere, 6, 1590-1607, doi:10.3390/atmos6111590.

> We were not aware of this publication and we included a reference to it.

Page 4, Lines 5-19: How hot does the interior of the CVI inlet become? Provide temperature information for the heated counterflow stream. Also, what are the flow rates used for the various streams of the inlet?

> The counter flow is not actively heated. The counter flow is made up by the so-called supply flow. The supply flow is guided to the CVI inlet tip, where it is divided to the sample flow (sucked back to the instruments) and the counter flow (going out of the inlet). The supply flow is prepared from compressed air inside the lab, i.e. the counter flow as well as the CVI interior is at room temperature and therefore markedly warmer than the probed cloudy air. The supply flow and thus the sample flow is filtered and dried to a dew point below -40°C, which is the main reason for the evaporation of the droplets as soon as they have passed the counter flow. Typical flow rates have been 12 L/min for the supply flow, 10 L/min for the sample flow and 2 L/min for the counter flow.

Page 5, Lines 23-27: Doesn't the sampling efficiency depend on the droplet size distribution in ambient air? If the droplet distribution is not held fixed, it seems as though some sizes may have better or worse sampling efficiencies. Discussion about this issue is warranted here.

Concerning the relevant experimental sampling efficiency, two different issues have to be considered. The sampling efficiency of the used CVI inlet itself was determined in the lab and is described in Schwarzenboeck et al. (2000). The cut-off curve is rather sharp with a droplet transmission from 0 to 100% within 2 µm. Thus the shape of the droplet size distribution has only a very small influence on the sampling efficiency. In these lab determinations of the cut-off curve all droplet trajectories are aligned to the CVI inlet orientation. This is the main reason why an aircraft-based CVI system typically has a 100% sampling efficiency above its lower cut-off diameter. In ground-based applications this is different. First, the CVI inlet needs to be installed inside a wind tunnel to achieve the required large wind velocities at the inlet tip. Second, a ground-based CVI is directed into the main prevailing wind direction. During HCCT2010, the CVI was centered in direction of the preferred wind sector (232°) for connected flow conditions (Tilgner et al., 2014). Thus, droplets with trajectories non-aligned to the wind tunnel inlet, due to horizontal and vertical wind fluctuations, will be lost. Moreover, there are droplets that make it into the wind tunnel but with still non-perfect aligned trajectories with respect to the CVI inlet. As a consequence these droplets are sampled but have contact with the inner surface of the CVI, so that the residual particle is lost. In order to account for these loss processes, the overall sampling efficiency of the CVI system is derived as explained in the text.

Table 1: clarify in caption what is meant by the various numbers of "+" and "-" in the last column.

We added an explanation to the table caption as follows:

The similarity between the trajectories for cloud events and non-cloud comparison times is given in the last column (+++: same air mass trajectories, ++: small deviations, +: large deviations, -: different air mass origin).

Figure 1: clarify how far back the trajectories go in time, and what the final ending coordinates and altitude are for the trajectories.

The trajectories go back 96 h in time, the final ending coordinates were 50.65N, 10.77E, at 500 m above model ground level.
We added this information to the caption of Figure 1:

Figure 1: Back trajectories calculated using HYSPLIT (Stein et al., 2015; Rolph, 2016) for all full cloud events (FCE) and the according cloud free periods. The trajectories go back 96 h in time, the end point is 50.65N, 10.77E, at 500 m above model ground level. Details of the trajectory calculations are described in the supplement to Tilgner et al. (2014).

Figure 3: It is unclear how to read the bars. Specifically, what are the two shadings indicative of on the bars labeled "int+res"? It is very difficult to analyze the results in this figure due to the inability to understand that important bar. Caption and figure should be improved.

We improved the explanation given in the figure caption. The shadings refer to the interstitial and residual mass concentration which are stacked in order to compare the sum of interstitial mass concentration and residual mass concentration ("int" + "res") to the out-of-cloud aerosol. This is now explained in the caption as follows:

Figure 03: Composition of cloud residual and interstitial particle mass concentration during the full cloud events (FCE) and particle mass concentration during corresponding non-cloud

times. Interstitial and out-of-cloud aerosol particles were measured using the HR-ToF-AMS, cloud residuals were analyzed using the C-ToF-AMS. The first bar shows the sum of the residual concentration ("res") and the interstitial concentration ("int"); residual concentration (darker colour) is stacked on top of the interstitial concentration (lighter colour).

Page 8, Line 6: change “that” to “than”

changed

Section 3.2.1: The authors should also incorporate into the discussion the recent results of a paper focused on this very issue: Prabhakar et al. (2014). Sources of nitrate in stratocumulus cloud water: Airborne measurements during the 2011 E-PEACE and 2013 NiCE studies, Atmos. Environ., 97, 166-173, doi:10.1016/j.atmosenv.2014.08.019.

We added the following to section 3.2.1:
In a more recent study, Prabhakar et al. (2014) concluded from aircraft-based measurements in clouds that dissolution of HNO_3 in cloud drops and nucleation scavenging of NO_3-containing particles both contributed to enhanced nitrate concentration measured in cloud residuals.

General comment: was there any evidence of influence from biomass burning in this study?

There was influence of biomass burning, this has been reported in Roth et al. (2016). AMS Data (Fig. 8 in Roth et al.) showed that at end of campaign up to 0.3 µg m^{-3} were attributed to biomass burning organic aerosol (BBOA) (inferred from "poor man's PMF"), while total organics were about 5 µg m^{-3} at that time. The single particle data presented in Roth et al. show that a large fraction of the particles (25-30%) both in the out-of-cloud aerosol and in the cloud residuals showed biomass burning signatures. However, the AMS data indicate that the mass concentration of BBOA was rather low: About 6% according to the "poor man's PMF" estimation in Roth et al.), and a very small contribution of f_{60} (marker for levoglucosan) in Figure 10 of our manuscript.

Page 13: Line 24-26: The authors should update their references here because more studies than they have listed have examined cloud residues using an AMS, with results that could be relevant to interpretation of their own results. Below are a few examples that should be included:

Coggon et al. (2014). Observations of continental biogenic impacts on marine aerosol and clouds off the coast of California, J. Geophys. Res., 119, doi:10.1002/2013JD021228.

Sorooshian et al. (2013). Observations of sharp oxalate reductions in stratocumulus clouds at variable altitudes: organic acid and metal measurements during the 2011 E-PEACE campaign, Environ. Sci. Technol., 47, 7747–7756, doi:10.1021/es4012383.

Coggon et al. (2012). Ship impacts on the marine atmosphere: Insights into the contribution of shipping emissions to the properties of marine aerosol and clouds, Atmos. Chem. Phys., 12, 8439-8458.

Wonaschuetz et al. (2012). Aerosol and gas re-distribution by shallow cumulus clouds: an investigation using airborne measurements, J. Geophys. Res., 117, D17202, doi:10.1029/2012JD018089.

Shingler et al. (2012). Characterisation and airborne deployment of a new counterflow virtual impactor inlet, Atmos. Meas. Tech., 5, 1259–1269.

Sorooshian et al. (2007). Particulate organic acids and overall water-soluble aerosol composition measurements from the 2006 Gulf of Mexico Atmospheric Composition and Climate Study (GoMACCS), J. Geophys. Res., 112, D13201, doi:10.1029/2007JD008537.

> We included these references to the discussion in section 3.2.3

Section 3.2.4: it may be worth mentioning that in a recent study (Below), an organonitrate species was found only in cloud water as compared to CDR and out-of-cloud aerosol owing to the effect of heat kicking the species out of the aerosol phase. The results of this particular study are indeed interesting and warrant future investigation as to the effect of temperature on CDR composition.

Youn et al. (2015). Dimethylamine as a major alkyl amine species in particles and cloud water: observations in semi-arid and coastal regions, Atmos. Environ., 122, 250-258, doi:10.1016/j.atmosenv.2015.09.061.

> This is an interesting aspect. In our single particle paper (Roth et al., 2016) from the HCCT project we reported that amine-containing particles were detected with enhanced abundance in cloud residues. However, DMA is not an organonitrate (but an alkyl amine), thus we think that this would be off-topic here.

General comment: What are the key sources of nitric acid, ammonia, and organics in the region? Also, what about organonitrates? Please add discussion about this.

> There are no large cities in the region, especially in the upwind direction (see list of cities within a 50 km radius around the measurement site in the supplement to Roth et al. (2016)). Thus, we expect the sources of organics and ammonia to be mainly from natural, biogenic sources, whereas nitric acid is most likely from NOx emissions (traffic or other) distributed over longer distances.

References

Prabhakar, G., Ervens, B., Wang, Z., Maudlin, L. C., Coggon, M. M., Jonsson, H. H., Seinfeld, J. H., and Sorooshian, A.: Sources of nitrate in stratocumulus cloud water: Airborne measurements during the 2011 E-PEACE and 2013 NiCE studies, Atmospheric Environment, 97, 166-173, doi: 10.1016/j.atmosenv.2014.08.019, 2014.

Rolph, G. D.: Real-time Environmental Applications and Display sYstem (READY) Website (http://ready.arl.noaa.gov), NOAA Air Resources Laboratory, Silver Spring, MD (last access: June 13, 2016), 2016.

Roth, A., Schneider, J., Klimach, T., Mertes, S., van Pinxteren, D., Herrmann, H., and Borrmann, S.: Aerosol properties, source identification, and cloud processing in orographic clouds measured by single particle mass spectrometry on a central European mountain site during HCCT-2010, Atmos. Chem. Phys., 16, 505-524, doi: 10.5194/acp-16-505-2016, 2016.

Schwarzenboeck, A., Heintzenberg, J., and Mertes, S.: Incorporation of aerosol particles between 25 and 850 nm into cloud elements: measurements with a new complementary sampling system, Atmos. Res., 52, 241-260, 2000.

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.: NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System, Bulletin of the American Meteorological Society, 96, 2059-2077, doi: doi:10.1175/BAMS-D-14-00110.1, 2015.

Tilgner, A., Schöne, L., Bräuer, P., van Pinxteren, D., Hoffmann, E., Spindler, G., Styler, S. A., Mertes, S., Birmili, W., Otto, R., Merkel, M., Weinhold, K., Wiedensohler, A., Deneke, H., Schrödner, R., Wolke, R., Schneider, J., Haunold, W., Engel, A., Wéber, A., and Herrmann, H.:

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