Answers to the reviewers

Referee 1

The 2010 cloud experiment at Mt. Schmucke (Germany) was performed with much effort and heavily instrumented with regard to cloudwater collection. This manuscripts describes a part of the data set (8 events, inorganic ions and DOC) and highlights three topics: The correlation between cloud concentrations and the liquid water content, the scavenging of substances by the cloud, and the cloud-droplet-size dependent concentrations of substances. Some parameters were measured with high time resolution, as two AMS systems were employed in the field. The results are manifold and described in great detail in this manuscript. The evaluation and interpretation of data was performed carefully yet clearly, results are embedded into the respective literature results. Overall, this is an interesting and precious data set. Although not breathtaking, this manuscript should be published in ACP. Some comments are intended to help the authors clarify some issues before final publication in ACP:

We thank the reviewer for his or her effort and thoughtful remarks and will reply to all comments in the following.

page 24320, line 26: Schneider (2015) is not a valid reference. Overall in section "2.2 Interstitial and residual particle sampling", there is no information about how efficient the separation between cloud droplets and interstitial aerosol is.

We removed the reference to the not yet submitted work and modified the sentence as follows:
"Details of the AMS measurements will be given in a forthcoming companion paper of this special issue (Schneider et al., in preparation)(Schneider et al., 2015)."

With regard to the separation between cloud droplets and interstitial aerosol: This is given in the Schwarzenböck et al., 2000, reference, where we refer the reader to for more details: Collection efficiency increases from 10% to 90% from approx. 4 to 6 μm.

page 24321, line 5: Poulain et al. (2015) is not a valid reference. The information of the monitor "for continuous (1 h time resolution) determination of water-soluble inorganic trace gases and particulate ions" is too sparse.

We removed this reference as well and added additional information on the MARGA system as follows:
"A full description of the instrumental setup will be given in a forthcoming companion paper of this special issue (Poulain et al., in preparation). In brief, a commercial monitor for aerosols and gases (MARGA 1S, Metrohm Applikon, The Netherlands) was used for continuous (1 h time resolution) determination of water-soluble inorganic trace gases and particulate ions. The MARGA operated at a sampling rate of 1 m^3 h^{-1} and consisted of a PM_{10} inlet, a wet rotating denuder absorbing water-soluble gases into deionised water (10 ppm H_2O_2 added as biocide), a steam jet aerosol collector to grow and collect aerosol particles, and 2 ion chromatography systems for online cation and anion analysis."

page 24322, lines 13-19: What about the stability of H2O2 and S(IV) during cloud water collection? These species may react with each other faster than within one hour, which is the time resolution of the cloudwater collection.

We agree that this can be a potential artefact, which is, however, difficult to address because it is a function of reactant concentrations and cloud water pH over the time of sampling. Observed concentrations of reactive species at the point of sample preservation can thus be more or less biased depending on actual cloud water conditions. To clarify this, we added the following sentence into section 2.5:

"Concentrations of reactive compounds at the time of sample preservation can be biased due to reactions during the collection period. The extent of such artefacts will depend on reactant concentrations and cloud water pH and cannot easily be estimated."

page 24323, line 19: Why three sites, didn't you talk about two sites only so far?

We haven't introduced the third site, because in this manuscript we don't present data from it. We understand this can be confusing, however, and have therefore changed section 2.3 from "Upwind site aerosol sampling" to "Valley sites aerosol sampling" and modified its beginning as follows:

"Next to the Schmücke in-cloud site, two more valley sites upwind and downwind of the Schmücke were installed during HCCT-2010 to characterise air masses before and after their passage through the clouds."

In addition, we added this sentence at the end of section 2.3:

"Data from the downwind site has not been used in the present contribution."

page 24327, line 6: van Pinxteren et al. (2015) is not a valid reference. As "Concentrations of a large number of organic acids were measured from the bulk cloud water samples", they need to be reported here. The ion balance (Fig. 2) should be complemented by the measured organic acid anions.

We removed the reference, but would rather not report the organic acid concentrations in detail in this manuscript. These data will be presented and discussed together with a range of other organics in a forthcoming manuscript. Including them here just for the ion balance would lead to duplicate publication. We agree, however, to give more details on the importance of the organic acids for the ion balance in the text and modified the paragraph as follows:

"Concentrations of a large number of organic acids were measured from the bulk cloud water samples and will be presented elsewhere (van Pinxteren et al., in preparation). Summing up the equivalent concentrations of the most abundant determined acids (formic, acetic, glycolic, oxalic, malonic, succinic, and malic acid) with consideration of their respective dissociation states depending on their pK_a values and sample pH values gives a range of 5 – 82 (average of 23) µeq L^{-1}, which explains 6 – 100% (average of 56%) of the inorganic anion deficit. In about 10% of the samples organic acid equivalent concentrations significantly exceeded the anion deficit (up to 255%), likely related to measurement uncertainties and/or non-determined cations. Considering that the DOC fraction likely contains many more than the analytically resolved organic acids, it can be assumed that the missing anions are predominantly organic in nature…"

Figure 3: Do symbols indicate the maximum concentration (CWL) datapoints?

The dots indicate data outside 1.5*IQR. We realise this information was missing and have now included it into the caption of Figure 3:

"…, whiskers extend to 1.5 IQR (interquartile range), and dots indicate individual data points outside this range."

page 24328, lines 19-23: This sentence is awkward and not clear. It may be deleted or, if considered important, be expanded in order to better explain the involved processes and conditions.

We agree and have deleted the sentence. The paragraph now reads:

"While LWC undoubtedly impacts solute concentrations, the additional variance it introduces to observed concentrations seems to be small, overall, and LWC does not seem to be the main driver in solute concentration differences during this study."

page 24329, lines 4-6: The sentence "Also in our dataset, LWC does therefore rather control the range of observable TICs than the actual TIC itself, : : :" is not very clear.

We agree and have deleted this sentence as well. The modified paragraph now reads:

"Maximum TICs are decreasing, while minimum TICs stay relatively constant with increasing LWC, leading to a range of observed TICs at any given LWC. As one and the same LWC value can result from different cloud microphysical conditions…"

page 24334, lines 25-29: The authors speculate about the potential role of organic acids in DOC behavior. They probably do know the answer, but do not present it to the readers of this manuscript. This is awkward.

We have checked our data and can tell that the determined main organic acids during the event discussed here (FCE11.2) explain less than 10% of the inorganic anion deficit. We can therefore not further elucidate the role of organic acids in DOC behaviour here. To indicate this to the reader, we have added the following sentence:

"It is noted that the main organic acids mentioned above explain only less than 10% of the inorganic anion deficit for this event."

sections 3.4.1 and 3.4.2: Please provide some information about the water volumes collected on the individual stages of the collectors. Wouldn't it make sense (despite all overlap between stages) to present LWC and CWL data as functions of droplet size?

We have added 2 figures in the supplemental material, giving water volumes per stage collected with the 3-stage (Fig. S8) and 5-stage collectors (Fig. S24). In addition, we added the following to the beginning of section 3.4.1:

"Volumes of cloud water collected per stage were between 5.9 and 240 ml with typically lowest volumes on the intermediate stage (16-22 μm) and highest volumes in the smaller or larger size class, depending on the sample (see Figure S8 for details)."

To the beginning of section 3.4.2, the following was added:

"Collected cloud water volumes were from 0.55 to 15 ml, with smallest volumes typically in the 4-10 µm droplet size range and largest ones mostly for droplets >30 µm (see also Figure S24)."

Tab 4 heading: Replace "> 0.2" by "< 0.2"

Thanks, done.

Referee 2

The present manuscript describes the chemical composition of clouds sampled during the HCCT-2010 campaign. It features an impressive dataset in terms of physical and chemical parameters (inorganic ions together with DOC) measured. The cloud sampling is performed using several cloud collectors allowing to analyze the cloud chemical composition as a function of the droplet size. Sampling of the interstitial phase and of the cloud water by the CVI/INT system allows estimating the scavenging of the chemicals by the cloud water. Finally, AMS measurements allow to evaluate the variability of the cloud water composition with a high time resolution. Such analysis of cloud chemistry is very rare and difficult and by themselves worthwhile additions to the scientific literature. The discussion of the results is very detailed but clear and organized in a logical way. Some results like the correlation between LWC and cloud concentrations are expected/traditional. Other approaches are rather novel. For example, the way you connect air masses collected at three campaign sites (connected air flow) is interesting and allows documenting "full cloud events". Factors controlling solute concentrations are more subject to debate since there are so many factors that can explain concentration variability... So certain of your conclusions are more or less speculative...
Overall the study is an interesting contribution to atmospheric cloud chemistry and I would support publication of the manuscript while encouraging the authors to consider the following comments.

We thank the reviewer for his or her comments and helpful remarks and will address all suggestions in the following.

1- The introduction part is too long and should be reduced. Too many details are present and need to be suppressed for more clarity. Most of the information in the introduction part is even discussed in the results part.

We agree and have removed two details in the introduction section on the control of solute concentrations, as well as omitted a large part of the discussion on solute concentration size dependencies from the Schell et al. modelling study.

2- p. 24319, line 12 : you argue that samples are stored at -20_C until analysis. For H2O2 analysis, this can lead to strong underestimation of the concentration. Indeed, the retention coefficient of H2O2 is below 1 (around 0.3 following Snider et al., 1992). This means that about 1/3 of aqueous H2O2 is retained in the crystal during freezing of the samples.

Actually, this is one of the reasons why H_2O_2 was stabilized/preserved immediately after sampling and prior to freezing, as described on P24322 L13-16 in the discussion paper.

3- p. 24321. Please notify the nature of the filters (teflon, nylon?).

The sentence was modified as follows:

"Cloud water from the different samplers was filtered through 0.45 µm syringe filters (IC Acrodisc 13, Polyethersulfone membrane, Pall, Dreieich, Germany) and analysed…"

4- p. 24324. Definitely, I think that CASCC2 bulk samplers are not fitted to collect successive cloud water samples... especially for trace ions. For FCE 1.1 and FCE 13.3, the concentrations of certain chemical compounds should be carefully considered. This leads also to a general comment. To my opinion, CASCC2 sampler concentrates the cloud samples due to the way they collect the water. I know that most of the cloud water collection are performed with this Teflon strands system but I prefer the system where droplets impact on flat surface. This leads to my question. Did you compare you measurements performed on cloud water collected by your various cloud water collectors (CASCC2 vs. 5 stage for example)?

Yes, we have compared both the 3-stage and the 5-stage concentration with the ones observed from the bulk CASCC2 collectors and did not find severe deviations. We didn't include it into the manuscript due to paper size reasons, but we agree that it is interesting information and have therefore now included two figures into the supplemental material showing volume-weighted mean concentrations from the multistage collectors plotted versus corresponding bulk concentrations (Fig. S3 and Fig. S4). In addition, we have changed the title of section 3.2 to "Control samples and collector intercomparison" and added the following paragraph at the end of this section:

"Comparisons of volume-weighted mean concentrations from the multistage collectors with bulk concentrations from the CASCC2 for main cloud water constituents (sulfate, nitrate, ammonium, DOC) are shown in Figure S3 and Figure S4. They reveal generally similar data between the samplers with a tendency of sometimes higher concentrations from the multistage collectors, which was, however, not consistently observed for all constituents and/or cloud events."

5- p. 24325. Your lowest value for cloud pH (3.6) seems really low. You need high concentration of strong inorganic acids (mainly nitrate and sulfate) to reach this value. If you compare for example with puy de Dôme measurements, you reach a pH value closed to 3.6 with significantly higher concentration of nitrate and sulfate. Please discuss.

A minimum pH of 3.6 does not seem extraordinary low to us, given that polluted air masses e.g. from the Rhine/Main area (Frankfurt/Main) can easily reach the rural Schmücke site. As reported by (Deguillaume et al., 2014), pH can reach even lower values in the polluted regime at Puy de Dôme. It is clear that higher concentrations of acids are needed for a pH in this range, but we would not consider this to be worth adding another discussion to the already quite long manuscript.

6- Conclusion. What is the next step? Modeling investigations to explain the results? Is it feasible with current cloud chemistry models? Please discuss.

The reviewer is right in assuming that the experimental data presented here will be used in our multiphase SPACCIM/CAPRAM model (actually has been used already, but data is not published yet). We have added the following as last bullet point to the conclusions section:

- "The comprehensive dataset obtained during HCCT-2010 will serve as a reference for the further development and evaluation of multiphase models in future studies."

Minor comments:
1- Please add in the table 1, pH values for each FCE.

Table 1 contains general information on the FCEs and is quite loaded already. We have added mean pH values to Figure 1, together with total solute concentrations, as suggested below.

2- Figure 1. Please indicate the total concentrations of measured chemicals for each FCE. This will help the readers.

Good point, done.

Reference: Snider, J. R., D. C. Montague, and G. Vali : Hydrogen peroxide retention in rime ice, J. Geophys. Res., 97 (D7), 7569–7578, 1992.

References

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