Atmos. Chem. Phys. Discuss., 12, C7340–C7353, 2012
www.atmos-chem-phys-discuss.net/12/C7340/2012/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Stable water isotopologue ratios in fog and cloud droplets are not size-dependent" *by* J. K. Spiegel et al.

J. K. Spiegel et al.

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Received and published: 24 September 2012

Final response to the comments from A.L. Rhodes

Our replies are given in blue color between the reviewer statements.

General Comments:
Reply: We would like to thank A.L. Rhodes for her comments, which helped to improve our MS.
Overall, this is a very good scientific contribution for ACP. The title of the manuscript summarizes the main finding quite clearly, and the methods and data analysis are

sound and well substantiated. The study aimed to test whether the assumption proposed by Bolin (1958) and later modeled by Jouzel (1986) — that droplets of different sizes within a cloud are in isotopic equilibrium with each other —could be confirmed by direct measurement. The study design addresses the question well, and the results show that differences in isotopic composition of cloud water are due more to the length of the sampling interval than to size of the cloud droplets. The presentation of the manuscript is good overall, and there are a few places, described in the next section, that can be improved for clarity.
Reply: We thank A.L. Rhodes for this positive feedback of our MS.
More notably, the study elicited additional questions for me that remained unanswered in the manuscript's discussion. For example, the study showed that the isotopic composition of cloud water varied significantly over different sample durations (e.g. Fig. 3). It makes sense that this could happen, but some explanation as to why could be helpful for many readers. For example, the "amount effect" might explain why isotopic values became lighter over the event duration if precipitation is occurring simultaneously. Was it raining during these events? The "amount effect" would not explain increasing isotope values, however. Would changes in temperature during the event explain them? Please see comment #6 in "Specific Comments" below that elaborates on this.
Reply: Cloud water was only collected during non-precipitating events. Consequently, the temporal variations most likely had different reasons than the amount effect. A detailed analysis of the possible drivers of these variations is presented in Spiegel et al. 2012. As we could not generally identify one driver (e.g. temperature) we decided to present the results in a different MS in order to keep the stories more compact and focused. We added more references in the MS to Spiegel et al. 2012:

- Added in caption Fig. 3: *Identification of the drivers of this temporal evolution as well as interpretation is presented in Spiegel et al. (2012).*
- Changed on p. 12673 l. 15. *Besides changes in local thermodynamic conditions,*

airmass history and transport as well as frontal passages could be identified as reasons for the temporal changes in δ values in the cloud droplets which are discussed in detail in Spiegel et al. (2012).

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Also p. 12665, lines 19-20, state "different droplet sizes could carry isotopic information from different locations in the cloud," based on the assumption that larger droplets typically are at the base of clouds whereas smaller droplets are higher. Do the authors feel their results address this statement?
Reply: Unfortunately, this statement is rather difficult to address from an experimental point of view. When sampling cloud droplets of a fixed location we always lack their history, meaning we do not know exactly where they were inside the cloud before being collected. It is mentioned in the introduction as a possible mechanism that could lead to different δ values in cloud droplets of different sizes. However, the aim of the paper was to address whether there were any differences at all.
In other words, do they know whether they are sampling different droplet sizes within one region of a cloud, or do the droplet sizes measured over the course of the event represent water collected from different regions in the cloud, which may have occurred if the cloud changed its elevation over the sampling interval?
Reply: A ceilometer was deployed downwind of the Schmücke measurement site. From these measurements we know that for some of the cloud events the cloud base varied over the whole event, while for some it stayed constant. However, the findings that the isotope ratio of the cloud droplets was independent of the droplet size, was independent whether we measured 250 m above cloud base or only 50 m.

The authors may not be able to answer these questions directly from the data, but the question posed in the introduction could be addressed.
Reply: We did not address this question in the MS but we added on p.12672 l.13: *Consequently, droplets basically immediately "forget" their isotopic information which*

they carry arriving from a different location in the cloud or as a result from longer droplet live times.
Furthermore on p.12673. l. 13: *This finding is in agreement with what we would expect from the equilibration times calculated for a single droplet illustrating that this simple model can be applied to a droplet ensemble.*

Some further discussion about the changes in composition over time is warranted, including the implications of this result, as well as proposing other questions for future work.
Reply: We addressed the consequences of our work for future studies in the conclusions. Additionally, we will add the sentence at the end of the conclusions:
Furthermore, to investigate the cloud's inhomogeneity, simultaneous measurements at different heights within in the cloud and the development of airborne collection techniques of cloud water for isotope analysis would be needed.
For example, one of the co-authors (Scholl) has written about isotopic differences between rain and cloud water collected during the same event. Do the "elapsed time" data in this manuscript relate to those prior observations in some way?
Reply: This is the first study resolving the temporal evolution of the δ value during one cloud event. So far, sampling intervals were basically event wise or on a monthly basis (tabulated in Scholl et al. 2010). So the duration was mostly longer than in our case.

Specific Comments:

1. p. 12664, Lines 11-15. The last 2 sentences of abstract state that observations of different isotope ratios for different cloud droplet sizes result from the collector scavenging cloud moisture at different moments in time, which may happen as the cloud dissipates. This interpretation also needs to be in the conclusion sec-

tion of the paper.
Reply: We included in line 21 on page 12674:
However, when the cloud dissipated the differences between droplet sizes tended to be larger, most probably reflecting different collection times of the respective droplet sizes.
The term “dissolution period of the cloud” needs to be defined in discussion.
Reply: See number 9 of the replies. Additionally, we add on p. 12664, l.12:
, when the supersaturation inside the cloud decreased and the cloud began to clear,

2. p. 12665, lines 25-29: A description of how the paper is structured is unnecessary because it follows the standard format of the journal. Better to replace this text with a summary of the main argument and evidence that supports the conclusion in the first sentence of the paragraph.
Reply: We agree and replaced: *In this study, we present the first experimental evidence that there is no difference in isotope ratios for different droplet sizes in hill cap clouds. The work is structured as follows. First, we present the measurement site and the sampling method, followed by the model of a single isolated cloud droplet. Then, the results are presented and discussed, conclusions are drawn, and recommendations are given for future cloud water sampling for isotope ratio analysis.*
by:
In this study, we present the first experimental evidence that there is no difference in isotope ratios for different droplet sizes in hill cap clouds dominated by liquid phase microphysics. The δ values of the cloud droplets of three different relevant size classes did not differ significantly.

3. p. 12667, line 12: Please define the term “50% size cuts.”
Reply: the 50% cut size is the droplet size at which the droplets are collected with 50% efficiency; larger droplets are collected with a higher efficiency and smaller

droplets with a smaller efficiency. We replaced:
We ran the CASCC with a volume flow of 19 m^3 min^{-1}, leading to 50 % size cuts (modeling result) at approximately 22, 16 and 4 droplet diameter for stages one, two and three, respectively (Raja et al. 2008). As droplets collected on adjacent stages overlap in size, measured composition differences are somewhat conservative estimates of actual differences in composition versus droplet size..
by:
We ran the CASCC with a volume flow of 19 m^3 min^{-1}. Based on modeling results presented by Raja et al. 2008, the expected 50 % size cuts for stage one, two and three were approximately 22, 16 and 4 , respectively. The term 50 % size cut corresponds to the droplet size at which droplets are collected with a 50 % efficiency; larger droplets are collected with a higher and smaller droplets with a smaller efficiency. Consequently, droplets collected on adjacent stages overlap in size and thus measured composition differences are conservative estimates of actual differences in composition versus droplet size.

4. p. 12671, line 6: Add the word “increasing” to clarify that the t99 decreased slightly with increasing temperature.
Reply: We included this in the revised MS.

5. p. 12671, line 19: The term “time” needs to be clarified as elapsed time.
Reply: Table 1 shows the result of two different types of two way ANOVAs that we performed with our data: while the ANOVA of the DI-samples was performed for all blank samples collected during the campaign, we performed the ANOVA for the cloud events for each cloud event separately. Consequently, the factor *time* is different for the DI-samples in comparison to the cloud samples and it would be therefore wrong to use elapsed time in this context. We agree with A.L. Rhodes that this is not clear from the table caption and we therefore changed the caption to:
F- and p-values for a two way ANOVA (factors: Time and Size) for the measured

δ^2H and $\delta^{18}O$ values for the six DI-samples and for each cloud event separately comprising more than one cloud sample. The factor Time is represented by the sample number within an event and was used as a categorical variable in the ANOVA. ***Bold*** *indicates that the null hypothesis needs to be rejected at a significance level $\alpha = 0.05$ (H_0 (events): Cloud water from all vials have the same δ values; H_0 (DI-samples): Water from all vials have the same δ values as the DI water). For events 1, 5, 7 and 12, the ANOVA was only performed for δ values from stage 1 and 3, as at least one δ value for the stage 2 was missing. As there were 18 independent tests necessary for the cloud events, we applied the Bonferroni correction (Legendre and Legendre, 1998) resulting in an adjusted significant level $\alpha_{adj} = 0.05/18 = 2.7 \times 10^{-3}$ against which the p-values were compared.*

Later in the paper, it is apparent that the elapsed time varies from collection period to collection period, but how the collection time is used in the statistics presented in Table I is not clear. Please elaborate how you tested significant differences between different times.

Reply: For the blank samples the factor time is the number of the blank sample (1, 2 to 6 as 6 blank samples were taken). As we were only interested whether the blank samples differ at all from the deionized water, it is appropriate to use the blank number as a measure of time. Time as a factor indicates that the different blank samples should not be interpreted as a numerical value. For the cloud events the factor time is rather the sample number during each cloud event than the elapsed time itself, which is not clearly written in the MS and has been changed in the revised MS as follows:

p.12671 l.19: *collection time (Time)* by *sample number (corresponds to the factor Time in Table 1)*

p.12673 l.3: *As the focus of the ANOVA was on the differences between droplet sizes, we chose both the elapsed time (Time in Table 1) and the collector stage (Size in Table 1) as factors.*

by

As the focus of the ANOVA was on the differences between droplet sizes, we chose both the Time within the event (Table 1) and the collector stage (Size in Table 1) as factors. Time was treated as a categorical variable represented by the sample number in our ANOVA. This means that we only tested whether time in the event has an effect on the overall variance in our data, neglecting the question whether the absolute time interval between samplings also has an effect.

We used this ANOVA in order to test the hypothesis whether there were any significant differences between droplet sizes. In order to point out what really means "significant" we wanted to compare the changes in δ values with respect to size to any random change that could happen. In this setup, we chose the change in time as a random change and therefore used the same ANOVA setup — meaning factors rather than variables — for both *time* and *size*. So for this test it is not relevant that the collection times of the different cloud samples differ, which in our eyes justifies the use of the sample number as a factor and measure of time.

6. p. 12672, first paragraph under section 3.3 (lines 6-14): Much of this could go in methods section, which would also help clarify statistical analysis presented in Table I.

   Reply: We moved this to the method section in the revised MS.

   Also, the reader is referred to Spiegel et al. (2012) to understand the temporal evolution of the isotope ratio during cloud events. That's fine if interpretation warrants a separate publication, however a summary of those interpretations is needed in this paper too (and the authors can refer to Spiegel et al. (2012) for the details and justification). A summary is needed so the paper will read more completely on its own because the variation in isotope ratio is very pronounced in the temporal data (as presented in Table I and Figure 3). Each paper should be able to stand on its own. It is okay to present summary of findings of the complementary manuscript.

Reply: see second point under general comments (repeated here for completeness):
"the temporal variations most likely had different reasons than the amount effect. A detailed analysis of the possible drivers of these variations is presented in Spiegel et al. 2012. As we could not generally identify one driver (e.g. temperature) we decided to present the results in a different MS in order to keep the stories more compact and focused. We added more references in the MS to Spiegel et al. 2012:

- Added in caption Fig. 3: *Identification of the drivers of this temporal evolution as well as interpretation is presented in Spiegel et al. (2012).*
- Changed on p. 12673 l. 15. *Besides changes in local thermodynamic conditions, airmass history and transport as well as frontal passages could be identified as reasons for the temporal changes in δ values in the cloud droplets which are discussed in detail in Spiegel et al. (2012)."*

7. p. 12673. I appreciated the presentation of the statistical analysis in the first paragraph on this page.
Reply: thanks for this supportive statement.

8. p. 12673, lines 21-26: Too much information is in this sentence. Rewrite to make less awkward, and to improve clarity.
Reply: We changed this sentence as followed in the revised version of the MS: *This was the case for the last cloud samples of event 10 and 11 (Fig. 3 and Fig. 4) as well as the sample of event 4*[1].

[1] *Only one cloud sample was collected during event 4 with the following δ values including standard errors for stage 1, 2, and 3: -72 ± 0.3‰, -74 ± 0.3‰, and -72 ± 0.2 (δ^2H) and -10.9 ± 0.02‰, -11.4 ± 0.03‰ and -11.0 ± 0.10‰ ($\delta^{18}O$).*

9. p. 12673, lines 27-28: Reference to Fig. 5c. Discussion needs to explain Figure 5 completely;
Reply: We changed p. 12673 l. 26 - p.12674 l. 9 in order to make the text clearer to
We selected event 11 as a model event to explain the process leading to larger differences between δ values of different stages at the end of a cloud event (see Fig. 5): The last cloud sample was collected during the dissolution period of the cloud (gray hatched area in Fig. 5c) which was characterized by a decreasing LWC during the sampling interval (gray line in Fig. 5c). As LWC remained $> 0\,g\,m^{-3}$, we assume that the air was still supersaturated with water vapor during sampling. Simultaneously, the effective radius R_{eff} increased (black line in Fig. 5c) indicating that the smaller droplets evaporate first when supersaturation decreases. Consequently, the cloud water of stage 3 was probably collected at the beginning of the sampling interval, while the other two stages continued collecting cloud water until the end of the sampling interval when smaller droplets had already disappeared (Fig. 5d). If we now assume that the δ^2H changed during the sampling interval (hypothetical δ^2H of cloud droplets in Fig. 5d), stage three represents a δ value from the beginning of the sampling interval, while the δ value of the cloud water collected in stage one and two is a mean value of the whole sampling interval, which could explain the observed difference. On the other hand, during sampling interval 2, LWC and R_{eff} stay rather constant (Fig. 5c), indicating that all stages collected cloud water continuously. So in all three stages, the measured δ value represents a mean value over the whole sampling interval 2 leading to a much smaller difference between the stages than during sampling interval 3 (Fig. 5a). For the last cloud sample of event 10, LWC and R_{eff} behaved similarly as described for event 11, indicating cloud dissolution and hence the same collection artifact. During cloud event 4, R_{eff} varied strongly during the whole sampling interval. Hence, we assume a rather inhomogeneous cloud and it is likely that the cloud water was not collected simultaneously in the

different stages for these cloud samples as well, as not all droplet sizes were present during the whole sampling interval.
it is difficult to understand from just the figure caption. In particular, I do not understand part d of Fig. 5 and what the hypothetical d2H evolution in cloud droplets represents.
Reply: We changed the caption of Fig. 5 to *Illustration of the collection artifact arising during the dissolution period of the cloud for event 11.* ***(a)*** $\Delta_{st}\delta^2 H$ *for all cloud samples of event 11 including the 1.8‰ threshold as a dashed line.* ***(b)*** *Sampling intervals of cloud sample 2 and 3 (1 is not shown).* ***(c)*** *Liquid water content (LWC) and effective radius* (R_{eff}) *measured with the Particulate Volume Monitor (PVM-100). The dissolution period of the cloud is indicated as a hatched area. (**d**, left axis) Collecting times (estimated from the measurements in panel **(c)**) for the three different CASCC stages and (**d**, right axis) hypothetical* $\delta^2 H$ *evolution in cloud droplets which could lead to the observed* $\Delta_{st}\delta^2 H$ *depicted in **(a)**. See Sect. 3.4 for detailed explanation.*
Also, make sure the acronym "LWC" (liquid water content) is defined previously in the paper.
Reply: Liquid water content is explained in the paper p.1266 ll.14

10. p. 12674, line 1: Clarify what "least saturated sampling conditions" means.
Reply: We replaced this by "saturated conditions during sampling" in the revised MS.

11. p. 12675, first paragraph. Please clarify use of term "evaporated' in this section. Readers could be confused, thinking that smaller water droplets in the collector may have evaporated, which would change the isotope ratios of the water (and account for the collection artifact this way). Instead, I believe the paper attempts to describe an evaporation process in the cloud that affects whether small water droplets are available to be collected. Be carefully clear in this section because readers need to understand the interpretation of the "collection artifact." This needs to be summarized in the conclusion section (e.g. my comment #1). The interpretation is reasonable; if evaporation in the collector occurred, the data should show a systematically higher isotope ratios for the small droplet size (which wasn't observed).
Reply: See number 9 of the replies

Technical Corrections:

1. p. 12665, line 1: removed "e.g."
Reply: We removed this in the revised MS.

2. p. 12672, line 20: expression measured in fog "so far" is awkward.
Reply: We changed *so far* to *in earlier studies.*

3. Figure 3. End of figure caption is missing a period.
Reply: We added this in the revised MS.

Final response to the comments from referee 2

Reply: We thank the second reviewer for his or her comments, which helped us to improve the quality of the manuscript.
The manuscript proves very convincingly that fractionation of isotopologues of water does not occur in a specific type of clouds. Very unusually, already the title all the manuscripts conveys the final conclusion of the work. While the statement in the title is well founded by the work presented in the manuscript, it might be deceiving since it does not refer to the restrictive limitations which are described inside the text (e.g. that only a specific type of warm clouds is investigated). Thus the title in itself seems to be an unquestionable axiom, which is not quite true. I suggest that the authors think it

over and perhaps come out with an alternative and less explicit title.
Reply: Although we think that a title should summarize the main message of the paper we agree that we should be more precise in the title and changed it to:
Stable water isotopologue ratios in fog and cloud droplets of liquid clouds are not size-dependent.
We also added *liquid* on p. 12664 l. 4 before cloud

The rationale behind the work is very clearly presented, starting from the importance of the question through early model efforts and experimental works to the definition of the main objectives. Although models and experiments unanimously suggest that fractionation is unlikely, there are some speculations about real-cloud processes that might cause fractionation of water isotopologues. Thus the experimental confirmation of the results of this very important field is highly invaluable. However, the detailed description of the entire structure of the manuscript is totally unnecessary in the final paragraph of the introduction.
Reply: We removed it in the revised version of the MS, see responses to A. L. Rhodes, specific comments 2.

The experimental setup of the work is very well founded and presented in the manuscript. The main conclusions of the manuscript are robust, including those regarding potential sampling artifacts in times of cloud dissolution. Although the work was done on a specific type of warm cloud (fog), the results suggest that physical processes in (warm) clouds do not lead to measurable fractionation of isotopologues. This is reassuring for the representatives of other fields who are relying on stable isotope measurements.

Specific comments:

The long sampling times may not be ideal for testing any potential cause of fractionation described in the introduction (e.g. different values in different locations in the cloud). Even if there are any such effects, they are likely averaged out during the sampling.
Reply: We agree with Referee #2 that a higher time resolution would be better to address faster processes. However, based on the theoretical approximations presented in Section 2.4, cloud droplets are supposed to equilibrate very quickly with the environment. So in order to address such processes size resolved sampling times needed to be on the order of seconds (t«t99) which can not be realized with the CASCC technique. Nevertheless, for future campaigns, shorter sampling intervals would be desirable.
There are significant differences in isotope abundances over the clouds' lifetime: I presume that such changes do not happen all at once. They start in different region of the clouds, temporarily affect different droplet sizes, etc. It is likely that much better temporal and spatial resolution would be needed to better understand the causes of these variations which are detailed in another manuscript.
Reply: We agree with Referee # 2 that a higher temporal and spatial resolution would be needed in future studies. However, we would like to point out that with ground based measurement techniques such as the CASCC technique, the collection of samples at different locations in the cloud at the same time is really difficult. Especially different heights above cloud base would be better achieved by airborne measurements. However, sampling techniques for airborne sample collections of cloud water for isotope analysis are missing. We added at the end of the conclusions:
Furthermore, to investigate the cloud's inhomogeneity, simultaneous measurements at different heights within in the cloud and the development of airborne collection techniques of cloud water for isotope analysis would be needed.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 12663, 2012.