Authors response to anonymous referee #2 on "Evaluation of a field-deployable Nafion™-based air drying system for collecting whole air samples and its application to stable isotope measurements of CO_2" by Paul, D. et al.

Dear Referee,

Thanks a lot for your valuable and constructive comments. We have revised our manuscript based on the comments we received. Through this document, we are addressing all comments we received, shown in *italic* font and our responses to them are shown in regular font (inserted texts are underlined).

In addition, there were some errors in the annotations of Figure 4 which has been updated (n in dry mode was 11 and not 12; standard error of the mean corresponding to $\delta^{13}C$ and $\delta^{18}O$ was changed to 0.013 and 0.005, respectively from 0.008 and 0.004).

Sincerely,

Dipayan

(on behalf of all co-authors)

Specific comments and technical corrections from https://www.atmos-meas-tech-discuss.net/amt-2019-295/amt-2019-295-RC2-supplement.pdf

- *Referee's comments on page 1:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 2:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 3:*

Authors response: All textual suggestions have been incorporated.

Comment #5: *use TM throughout ms*

Authors response: "Nafion" has been changed to "Nafion™" throughout the manuscript.

- *Referee's comments on page 4:*

Authors response: All textual suggestions have been incorporated.

Comment #1: *define all acronyms at first use*

Authors response: We have now expanded all the acronyms.

Comment #2: *Based on your own measurements?*

Authors response: To address your question regarding the source of the indicated measurement precision, we have added the following text for clarification. Additionally, we have also corrected our text, as pointed

out by Referee #1, which now indicates the measurement precision of CO_2, CH_4 and H_2O (and not CO, which Picarro G2301 doesn't measure).

"…The overall measurement precision of the CRDS-systems used was typically <0.03 μmol mol^{-1} (ppm) for CO_2, <0.2 nmol mol^{-1} (ppb) for CH_4, based on our long-term measurements of target cylinders, and <30 ppm for H_2O, based on manufacturers specifications."

- *Referee's comments on page 5:*

Authors response: All textual suggestions have been incorporated.

Comment #2-3: *type?; you should have all the relevant components listed, with model etc. - best in a Table*

Authors response: We have added all the relevant component part numbers within the text.

- *Referee's comments on page 6:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 7:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 8:*

Authors response: All textual suggestions have been incorporated.

Comment #1: *per flight/sampling/....*

Authors response: The sentence has been rephrased to: "For the ASICA project, typically 12 flasks are filled with dried air during each flight sampling."

Comment #2: *do you mention somewhere if this is absolute or above ambient?*

Authors response: We have inserted the word "absolute" to make the filling pressure explicit and the sentence reads as: "A sample is collected by closing the downstream flask valve and pressurizing the flask to 275 kPa (absolute) before closing the upstream valve (corresponding to ~1.9 L of air at STP)."

Comment #4: *it would be good if you could cite a reference here*

Authors response: During the initial stages of this work, we tested $Mg(ClO_4)_2$ as a desiccant and its effect specifically on the stable isotopic composition of CO_2. We did not observe any significant deviation in CO_2 mole fraction and its stable isotope composition ($\delta^{13}C$ and $\delta^{18}O$) caused by $Mg(ClO_4)_2$.

Comment #5: *not correct, it is a strong oxidizer - it supports combustion*

Authors response: This sentence has been rephrased to: "Perchlorates are stable at normal temperatures, but when they are exposed to high temperatures e.g. in case of a fire, they accelerate combustion."

- *Referee's comments on page 9:*

Authors response: All textual suggestions have been incorporated.

Comment #6: *you should add a statement about if and how the 3A mol. sieve works/alters the composition of the gas.*

Authors response: We have added the following text based on our own experience: "Although an excellent desiccant by itself, molecular sieve (type 3A) cannot be used to directly dry sample air as it tends to alters the composition of air. Hence, we chose to use molecular sieve (type 3A) as a drying agent in the purge flow line because it is additionally non-toxic, economical, and reusable."

Comment #11: *- 2 or +2?*

Authors response: +2°C is correct.

- *Referee's comments on page 10:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 11:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 13:*

Authors response: All textual suggestions have been incorporated.

Comment #2: *please comment/explain why the test is still valid even if you did not go to ~ 4 %vol H2O*

Authors response: We have added the following text "… Although the humidity level achieved in these experiments were less than the maximum one would encounter in the Brazilian Amazon (0-3 km), it clearly demonstrates the lack of isotopic exchange caused by the interaction of CO_2 with the oxygen-rich Nafion™ surface in the dry mode and in a relatively less severe wet mode. Indeed, further experiments with sample air saturated with water vapour, up to ~4 %, would be needed to confirm a complete lack of isotopic exchange even at high-humidity conditions."

- *Referee's comments on page 14:*

Authors response: All textual suggestions have been incorporated.

Comment #2: *true for lab test/conditions - but this does not explicitly confirm that at ~12L/min this still holds - has to be demonstrated/discussed*

Authors response: We agree with this comment that the presented experiment does not explicitly show that the effect on the stable isotopic composition of CO_2 is insignificant even at 12 L/min. The reason this experiment was performed at a flow rate significantly lower than 12 L/min was to measure more discrete samples while processing ~300 L of air: had the experiment been performed at 12 L/min, the experiment would have yielded only 4 isotopic values in each mode (dry and wet) compared to 11 in the presented experiment. Additionally, we also expect that the extended residence time in the NAD (at 4.5 L/min) would allow more time for interaction of CO_2 with the NAD surface and thus introducing larger biases.

We have hence added the following sentence: "This clearly demonstrates that under laboratory test conditions the NAD has negligible effect on the isotopic composition of CO_2, even with significantly longer residence times in the Nafion™ tubes. It is thus expected that at higher flow rates (12 L/min), the reduced interaction time between the air stream and the NAD surface should have even lesser influence on the isotopic composition of CO_2."

- *Referee's comments on page 15:*

Authors response: All textual suggestions have been incorporated.

- *Referee's comments on page 16:*

Authors response: All textual suggestions have been incorporated.

Comment #2: *which compatibility goals (I know it is the WMO goals, but this is not clear from this portion of the text)*

Authors response: We have revised this part and the text reads as follows: "In these experiments, we tested 4 different conditions by filling a set of three flasks under the following conditions: (A) dry air-without dryer, (B) dry air-with dryer, (C) wet air-without dryer, and (D). wet air-with dryer. When the difference between the base condition and the test condition remained within the WMO recommended compatibility goals (±0.1 and 0.05 ppm for CO_2 for the Northern and Southern Hemisphere, respectively; ±2 ppb both for CH_4 and CO; ±0.1 ppb for N_2O; ±0.02 ppt for SF_6; ±0.03 ‰ for $\delta^{13}C$ and ±0.05 ‰ $\delta^{18}O$ (GAW Report No. 242, 2017)), we concluded that the test condition did not induce any significant bias to the measurement. With respect to applying these WMO compatibility goals it should be mentioned that these precisions should be seen as the scientifically desirable level of compatibility for concurrent measurements of well-mixed background air by different laboratories, while they may not be the currently achievable best 1-σ measurement uncertainty (GAW Report No. 242, 2017)…"

Comment #3: *This may be, but this does not in itself mean that the performance of these two systems is equal. Please elaborate a bit more - make it clearer what you want to say when mentioning this.*

Authors response: Indeed, the performance of the two Aerodyne TILDAS systems are not alike and are currently being evaluated. These performance characterizations would be described in forthcoming publications and hence, we have removed this part of the text.

- *Referee's comments on page 18:*

Authors response: All textual suggestions have been incorporated.

Comment #1: *I am missing just a bit more detail (independent from the manufacturer information) on the influence of (humid) nafion membrane on the CO2 concentration of the sampled air.*

Authors response: We have added a few more sentences, in the Discussions and conclusions section, to provide more details on the influence of the NAD on CO_2 mole fraction determination in samples.

"Since unbiased measurements of CO_2 mole fraction and its isotopic composition in whole air samples demand collection of very dry sample air, we tested and present here the results of a Nafion™ based drying system. Nafion™ dryers are an excellent alternative to chemical and recirculating chiller based dryers for mobile sampling platforms. For example, most chemical dryers either alter the chemical composition of the sample air, or are considered hazardous from a safety standpoint, especially when they are used onboard an

aircraft. On the other hand, recirculating chiller based dryers are very efficient but are large and extremely energy demanding, which makes their usage on light aircrafts logistically undesirable. Nafion™-based drying systems offer a consumable-free, reusable, and a field-deployable alternative, which does not necessitate incorporating hazardous chemicals and also eliminates the use of any power onboard an aircraft. Initial laboratory tests, using the Picarro G2301 analyser, already indicated that a Nafion™ based system did not alter the mole fraction of CO_2 and CH_4 in dry and humidified air samples and hence could potentially be a promising alternative. In this work, we tested the NAD which is configured for use with the PCP-PFP system from NOAA-ESRL, although the use of our system is not limited to that sampling platform.

…

The next requirement was to establish if the NAD was inert for the gases-of-interest and did not alter the isotopic composition of CO_2 while sampling. To understand the effect of the NAD on the isotopic composition of CO_2, we performed a semi-continuous zero-enrichment experiment with the TILDAS-SICAS instrument in our laboratory. In such an experiment, the same gas is treated both as a reference and a sample gas, where the reference stream is unprocessed and the sample stream is processed. Thus, a zero-difference between the reference and the sample stream would indicate that the processed gas was not modified at all. This is demonstrated in Figure 4, where the first part of the experiment shows that the isotopic composition of CO_2 is unaltered when dry sample air is passed through the NAD relative to the direct measurement of the dry sample air. The second part of the experiment demonstrates that the isotopic composition of CO_2, as observed when wet sample air is passed through the NAD (thus dried) relative to the direct measurement of the dry sample air, remains within the measurement uncertainties and thus indistinguishable. Since the TILDAS-SICAS is not designed for continuous measurements, we performed this experiment at a lower flow rate than what would otherwise be used in field to obtain more discrete measurements while processing a certain volume of air. This demonstrates that, even with a doubling of residence time in the NAD compared to field conditions, the isotopic composition remains unaltered. Therefore, shorter residence times during field measurements would reduce the chances of interaction between CO_2 and the wet membrane surface and would therefore be more favourable. Additionally, this experiment also clearly demonstrates that CO_2 mole fraction determinations are not significantly affected in the presence of NAD, in both dry and wet modes (sample) when compared to measurements performed without the NAD (reference). …"

- *Referee's comments on page 19:*

Authors response: All textual suggestions have been incorporated.

Comment #1-3: *please be more specific; please be more specific; I think you would do your setup more justice, if you did not limit it here to the utilisation in Brazil - even if it was constructed for this purpose. It can be used in many other settings.*

Authors response: We have added text to make this section clearer and read as follows: "We performed a storage stability check over a period of one month and the results indicated that the NAD, if stored in dry conditions i.e., filled with dry air immediately after conditioning, would perform similarly to one freshly conditioned. This was concluded by comparing the water removal capacity of the NAD and the lowest achievable water vapour concentration while processing ~200 L of humidified air (~2 %) at similar flowrates. This property is particularly beneficial for the sampling conditions in Brazil because the conditioning step is performed in the lab few days before the PFP and the NAD are shipped to the sample collection site. As such, the application of this drying unit is not only limited to sampling in Brazil, but can also be used in any other situation where drying large volumes of air samples is necessary and availability of electricity is an issue."

- *Referee's comments on page 20:*

Authors response: All textual suggestions have been incorporated.

Comment #1: *There are differences, albeit small - therefore rather, for example, the differences between the different experiments are in the range of measurement uncertainty*

Authors response: This sentence has been rephrased to: "... The second part of the experiment demonstrates that the isotopic composition of CO_2, as observed when wet sample air is passed through the NAD (thus dried) relative to the direct measurement of the dry sample air, remains within the measurement uncertainties and thus indistinguishable."

Comment #2: *It would make a more complete discussion if you elaborated in a bit more detail on this point (i.e. why is a shorter residence time even more favorable, what are the processes involved, surface processes, kinetic fractionation, etc.)*

Authors response: We have added the following sentence: "…This demonstrates that, even with a doubling of residence time in the NAD compared to field conditions, the isotopic composition remains unaltered. Therefore, shorter residence times during field measurements would reduce the chances of interaction between CO_2 and the wet membrane surface and would therefore be more favourable."

Comment #5: *I am unsure about the AMT policy this regarding, but my conviction is that all data used in a paper have to be freely available/deposited in a repository which is freely accessible, independently of the authors.*

Authors response: We now have the data freely available at https://hdl.handle.net/10411/XIDZEA.

- *Referee's comments on page 23:*

Authors response: The reference has been updated to: "Zellweger, C., Steinbrecher, R., Laurent, O., Lee, H., Kim, S., Emmenegger, L., Steinbacher, M., and Buchmann, B.: Recent advances in measurement techniques for atmospheric carbon monoxide and nitrous oxide observations, Atmospheric Measurement Techniques, 12, 5863-5878, 2019."