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Atmospheric
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Interactive comment on "Continuous measurements of methane mixing ratios from ice cores" *by* C. Stowasser et al.

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Answer to referee 2 comment on amtd-5-211-2012

We thank the reviewer for her/his careful reading of the manuscript, and for many useful comments.

1

Referee #2: Page 212, Lines 19 – 25 (Introduction). Can you please indicate the required analytical parameters (e.g. accuracy, precision, dynamic range, time response)

for continuous ice core measurements of methane?

Stowasser et al.: Required time response of the analytical system depends strongly on the depth of the ice and the location of the drilling site. In our study we have shown that the time response of our analytical setup is sufficient to resolve all climatically relevant variations as preserved in the ice down to a depth of 1980 m in the NEEM core. Such an assessment of system time response should be done for every study individually.

However, we state on p.213, l.1-3, that one needs to capture variability on the scale of decades to centuries. This cannot be translated into a length without knowing the depth-age relationship of the ice core that is analyzed.

With GC technology accuracy and precision are of the order of ±10 ppbv. Generally it can be said that with better precision and accuracy new features of the CH_4 record become visible. We know this from ongoing projects. Therefore the required accuracy and precision is a moving target and one can say the lower the better. As an example we decided to mention the interhemispheric gradient of methane and included the following into the introduction:

"CH_4 mixing ratio measurements need to be of high precision and accuracy to resolve small details in the records, such as the interhemispheric gradient (IHG) that reflects the latitudinal source distribution. The IHG, obtained by comparing Greenlandic and Antarctic records, is as small as 15 ppb during glacial conditions (Dällenbach et al., 2000), requiring a combined precision and accuracy of ±5 ppbv."

The dynamic range of a spectrometer suited for ice core CH_4 mixing ratio measurements should cover glacial, interstadial and preindustrial CH_4 mixing ratios, i.e. mixing ratios between 300 to 800 ppbv.

Added information about dynamic range in introduction, p.212, l.21: “Records obtained from ice cores show CH_4 variability of ca. 300 to 800 parts per billion by volume (ppbv) over the last 800 kyr both on both the orbital time scale of glacial-interglacial cycles [Loulergue2008], and on the millennial time scale of abrupt Dansgaard-Oeschger cycles [Chappellaz1993].”

2

Referee #2: Page 215, Lines 21 – 25. If possible, please quantify the dependency of the membrane extraction on water pressure, air pressure, and temperature. Likewise, please quantify the dependence of the dissolved methane concentration on these parameters (e.g. P, T). This is critical in assessing how well the pressures and temperature must be controlled to obtain adequate precision and minimal bias.

Stowasser et al.: This is unfortunately not possible at this time. By holding all these parameters as constant as possible we are able to obtain good results. However, tests of the effect of temperature, water and air pressure on the gas extraction module, as well as the effect on CH_4 mixing ratios are planned, but have not been conducted yet.

3

Referee #2: Page 215 – Page 216. Can you quantify the efficiency of the membrane extractor at your flow rates and conditions?

Stowasser et al.: At the given flow rates and conditions the gas extraction module removes all bubbles (visible gas) from the sample stream. The pressure gradient over the membrane has been adjusted to 300 mbar in order to guarantee that all bubbles are extracted.

We did not quantify how much of the dissolved gas is removed at the given conditions. Surely the higher the pressure gradient the more dissolved gas is removed. To circumvent a potential pressure correction, we try to keep temperature and pressure gradient constant also during calibration.

We added the following sentence on page 215-216: “This results in a pressure gradient of approximately 300 mbar across the hydrophobic membrane of the module, which is sufficient to extract all visible air from the sample stream.”

4

Referee #2: Page 216, Line 12. Please confirm that the sample is dried to 0.003 % (30 ppmv). Typically, Nafion does not dry to below 300 ppmv using the configuration described in the text.

Stowasser et al.: To answer this comment we performed a zero-check with the instrument using high-purity nitrogen (H_2O < 3 ppm). The instrument measures the water vapor concentration to be ca. 0.001 %V, suggesting that the measurement in the field was approximately correct. Unfortunately, the instrument has been modified a lot since the field season and we cannot guarantee that the water vapor measurement is unaffected by these modifications.

Leckrone et al. (1997) described the efficiency of Nafion drying under various conditions. According to their findings the minimal length for efficient drying at our sample flow rate of 1.6 ml/min is about 1 meter (temperature of ca. 23 degC, purge gas nitrogen). Also, the outer purge flow needs to be 8-10 times larger than the inner sample flow. For these conditions Leckrone et al., reported water vapor concentrations after the Nafion dryer as low as 13.1 ppmv.

Our nafion dryer is 2 m long and the outer purge flow is 8-10 times larger than the inner flow. Based on this, we conclude that our statement is in fact correct and decided to leave the reported water vapor concentration of ca. 30 ppm in the revised manuscript. However, if we interpret the work of Leckrone wrong, or if the referee has more information, which confirms that drying below 300 ppm is not possible, we will remove the reported concentration of 30 ppm from the manuscript.

5

Referee #2: Page 217, Line 5. Do the calibration gases also contain Argon? Argon significantly broadens the methane absorption spectra and should be included in the calibration source. If not, this may be one source of the observed bias offset.

Stowasser et al.: The field calibration gases do not contain Argon. The full-air standards from NOAA used for the calibration shown in Fig. 2b, do contain Argon.

It turned out that the manufacturer Picarro knows about this effect and quantified it

recently (C. Rella, personal communication):

“I don’t think Argon can be the answer – removing Ar and replacing it with air would cause an error of about 0.06 ppb at 600 ppb of CH_4. The effect is magnified at low cavity pressure, but I would estimate the error to be 5-6X, which is nowhere close to the 20 ppb error you are talking about.”

The lack of Argon in the field calibration gases can account only for a small part (< 1 ppbv) of the 20 ppbv bias. We included in following paragraph in bias discussion of the revised manuscript:

“Finally, the calibration gases used during the field campaign (see Fig.2a) are synthetic air standards, which do not contain Argon. Argon broadens the absorption spectra of CH_4 and a lack of Argon in the calibration gas introduces a measurements bias. According to the manufacturer, the magnitude of this effect is less than 1 ppbv at CH_4 mixing ratios of 600 ppbv and, thus, can only account for a small part of the bias found in our measurements.”

6

Referee #2: Page 217 – 218, Figure 2. The text should be revised to explain several aspects of these calibration curves:

a. Figure 2b. Please add a residual to the fit so that discrepancies from the line can be clearly seen. Moreover, the fit seems highly linear, thus, the large uncertainty in the slope (0.7941 ± 0.3561) is almost impossible. I assume that this a typographical error?

Stowasser et al.: As requested, we now give the residuals for the three data points in the figure.

Yes, it was a typographical error. The values for Fig.2b are: a = 0.7941 ± 0.0006 and b = -0.1258 ± 0.5967.

Referee #2: b. Figure 2a. There is a LARGE discrepancy between the slope in Figure 2b and Figure 2a. The instrument reads almost 16 % less methane than it should based on the pure gas calibrations. It is critical to discuss the sources of this low reading. Is the membrane extractor inefficient? Is there a substantial amount of methane still left in the water? Is it an instrument issue? Likewise, it is almost impossible for these spectroscopic instruments to have a non-zero intercept (the intercept is typically < 1 ppbv). Thus, the observed 12 ppbv offset is highly improbable, suggesting that the calibration response is non-linear and more standards are required. Please discuss these issues and possible reasons for this behavior in the text.

Stowasser et al.: We believe that the significantly lower methane values are mainly due to the solubility of methane and in water. A quick calculation shows the significant solubility of CH_4:

With the solubility of CH_4, L(CH_4), in H_2O at 20degC:

$$L(CH_4) = 22.7\frac{mg}{L(H_2O)\cdot bar}. \tag{1}$$

With the density of CH_4 of 0.6556 $\mu g/mL$ the solubility per mL is:

$$L(CH_4) = 0.0346\frac{mL}{L(H_2O)\cdot bar}. \tag{2}$$

The partial pressure of 400 ppb CH_4 (the mixing ratio in one of the calibration gases) in air at 1 bar is

$$p(CH_4) = 1bar\frac{400ppb}{1\cdot 10^9 ppb} = 4\cdot 10^{-7}bar. \tag{3}$$

The solubility of CH_4 in water for the given partial pressure of CH_4 is

$$L(CH_4)^* = 0.0346\frac{mL}{L(H_2O)\cdot bar}4\cdot 10^{-7}bar = 1.38\cdot 10^{-8}\frac{mL}{L(H_2O)}. \tag{4}$$

During calibration runs 1.6 mL of standard gas are mixed with 15 mL of water. In the 15 mL water of the calibration mixture x mL of CH_4 are dissolved:

$$x = 15mL\cdot L(CH_4)^* = 2.07\cdot 10^{-7}mL. \tag{5}$$

In the 1.6 mL air of the calibration mixture y mL of CH_4 are present:

$$y = 1.6mL\cdot\frac{400ppb}{1\cdot 10^9 ppb} = 6.4\cdot 10^{-7}mL. \tag{6}$$

The ratio of x/(x+y) is 24%, i.e the mixing ratio of methane in the bubbles is at equilibrium depleted on the order of 20%.

The gas extraction unit extracts some, but not all of the dissolved CH_4 molecules. E.g. Huber et al. (2003) used a similar membrane for continuous gas extraction (same fabric, but much smaller surface) and extracted 18-25% of the dissolved gas. On the other hand, as discussed on p. 225, l.16-24, the deionized water used for calibration is saturated with N_2, has the potential to lower the CH_4 mixing ratio of the calibration gases by up to about 15%. Considering the sum of these effects, we believe that the 16% less reading mainly due to the solubility of CH_4 are feasible.

In a way one could say that the gas extraction module is inefficient, since it does not extract all dissolved CH_4 molecules from the water. However, we did not expect the gas extraction module to extract all dissolved CH_4 molecules, which is why we kept temperature and pressure stable around the gas extraction module and, furthermore, tried to mimic the way the ice core sample runs through the system as closely as possible with the calibration mixture.

In the paper on p.9 we refer to the estimation above. We decided to refer to the estimation instead of including it into the paper, since it is more like supplementary information and will disturb the fluency of reading, if included in the paper.

Regarding the non-zero intercept:
A non-zero intercept could point to leaks in our front-end. Unfortunately, we did not have zero air during the field campaign to force the calibration curves through zero. We included the following two paragraphs at the end of the calibration Section 2.1:

"Figure 2a shows that the WS-CRDS in combination with the front end measures significantly less CH_4 compared to the stand-alone instrument as shown in Fig.2b. This is a result of the solubility of CH_4 in water: Before the measurements of the WS-CRDS in combination with the front-end, the calibration gas has been in contact with water from the moment when it was mixed with deionized water until it reached the gas extraction module. A significant amount of CH_4 molecules are dissolved in the water and are not completely extracted by the gas extraction module. An estimation of the amount of dissolved CH_4 molecules can be found in Stowasser et al. (2012).

The intersect of almost 12 ppbv in Fig2a suggests a leak in the front-end or, alternatively a non-linearity in the calibration curve. Neither a leak in the front-end, nor non-linearity of the calibration curve could be checked during field measurements due to the lack of a third calibration gas and a CH_4-free gas, respectively."

Referee #2: c. The authors conclude that the data presented in Figure 2b are more accurate partially due to the wider dynamic range of calibration. This is not true. The instrument calibration should span the measurement range as closely as possible. This accounts for the slightly non-linear response of the analyzer over a wider dynamic range. Thus, although there is less uncertainty in the slope of the fit line with a wider dynamic range, the accuracy of the instrument over the measurement range is worse. So, it is not true that using larger differences in the CH_4 mixing ratios in the field would improve the instrument accuracy.

Stowasser et al.: We deleted the paragraph mentioned.

Referee #2: d. Was the instrument zero checked (e.g. on dry nitrogen or similar)? If so, why weren't the calibration curves in Figure 2a and 2b forced through zero?

Stowasser et al.: It was not zero-checked.

Referee #2: e. Please note that it is critical to address these calibration issues (specifically point 6b above) in order for rest of the data to be interpreted.

Stowasser et al.: We agree that those are critical questions. Some need to remain open at this time, as additional tests need to be performed.

7

Referee #2: Page 219 – 220 (Figure 3). Please add a few more details to the stability plot and discussion:

a. The noise present in Figure 3a is clearly not "white noise" and shows discrete "drop-out" behavior. Why do you observe these sporadic, low readings?

Stowasser et al.: As it turned out after the field campaign the pressure reading of the instrument showed a bias of several mbar. Thus, the instrument did not operate at the exact cavity pressure for which the spectral fit was designed. We believe that the "drop-out" behavior is caused by this discrepancy.

We added the following to the caption of Fig.3:
"Outliers in the CH_4 mixing ratio measurement are the result of a discrepancy between operating pressure and fitting routine (see Section 2.4.2)."

In Section 2.4.2 "Cavity pressure and fitting routine" we added:
"After the field campaign it turned out that the pressure reading of the WS-CRDS had a bias of several mbar. Thus, the custom-designed spectral fit did not match the operating pressure. This caused outliers in the CH_4 mixing ratio measurements as shown in Fig.3a (green line). The red line in Fig.3a shows measurements without outliers: During these measurements the instrument was running in its original mode

with a cavity pressure of 225 mbar and the corresponding spectral fit."

Referee #2: b. Can you please overlay the pure gas data discussed on Page 219 (Line 22 onwards) onto Figure 3? This would help the reader see the differences in the Allan variances and raw data.

Stowasser et al.: Found a typographical error on p. 219, l. 7: It is 1h not 7h.

We overlaid the pure gas data and adjusted the text and figure caption accordingly. We decided to show only 50 minutes (out of 3.5 days) of the pure gas data time series to visualize that no drop-outs can be observed in this time series. During this measurement the analyzer was running in its original configuration with a cavity pressure of 225 mbar and the corresponding spectral fit. The Allan plot of the pure gas data is shown over the full time period of 3.5 days.

Referee #2: c. You conclude that the instabilities are due to the "gas extraction module"...can you elaborate on this conclusion? Is it due to a change in the membrane efficiency?

Stowasser et al.: Not at the moment. More tests are necessary before we can determine the cause of these instabilities. A change in the efficiency is a potential reason. One would expect a loss in efficiency with time, since dust particles from the sample could clog the pores of the hydrophobic membrane. A longer stability test is necessary to observe long term effects like this. Our guess (untested) is that fluctuations in the pressure at the gas extraction module cause the instabilities. These pressure fluctuations could be due to changes in the water-to-gas ratio of the sample stream (e.g. caused by degradation of pump tubing or temperature effects in the gas and water delivery system). They would affect the efficiency of the gas extraction module.

Referee #2: d. Since the calibration interval is 24 hours, can you estimate the 24-hour precision of the setup? It seems that providing a short-term Allan Variance (e.g. < 1 hour) is not relevant to the actual measured data presented in this paper.

Stowasser et al.: We cannot provide a stability test over 24 hours. During the field campaign we had not enough time to conduct these tests. Certainly, such a test would be very interesting.

Referee #2: e. You also conclude that the WS-CRDS is using software signal smoothing to improve the short-term precision to below the Allan variance limit. Did the manufacturer provide any further information about this point? How does this smoothing affect linearity?

Stowasser et al.: We did not receive further information on this topic. However, the manufacturer claims linearity of their instruments. Linearity for the stand-alone instrument was also confirmed for our spectrometer (Fig.2b). However, due to our complex front-end non-linear effects may occur that are not related to the instrument.

8

Referee #2: Page 222, Line 9. Can you estimate the orifice size of the needle valve?

Stowasser et al.: The orifice size is 0.81 mm (Information from manufacturer

Swagelok). Added the information to the text.

9

Referee #2: Page 222, Line 24. Please note that CH_4 does NOT interact with the cavity surfaces in any significant way. The observed smoothing is largely dominated by flow response time and dispersion.

Stowasser et al.: We removed the statement that CH_4 molecules interact with surfaces.

10

Referee #2: Page 223, Line 7. Cavity-enhanced absorption spectrometry techniques must retain very clean flows to prevent fouling of the cavity mirrors. Yet, you removed the inlet filter. Was the gas pre-filtered in another manner? Did the cavity foul (i.e. get dirty)? What happens if it does?

Stowasser et al.: We removed only one of the two high-purity filters (removal rating $\geq$ 30nm) that are located upstream of the cavity to protect the cavity from contamination. We replaced this filter with a 0.5 μm filter from VICI that has a much smaller internal volume. This filter does some pre-filtering when the sample enters the spectrometer. Other than that, no pre-filtration takes place. We did not observe an increase in the CH_4 baseline, which would occur in case of contamination.

We added the information to the text:
“The internal volume of the WS-CRDS is reduced by switching to small-diameter

tubing throughout the spectrometer. Furthermore, we removed a high-purity gas filter at the inlet of the spectrometer (Wafergard II F Micro In-Line Gas Filter, Entegris Inc.). The cavity is still protected from contamination by a second, identical filter upstream of the cavity. As a replacement for the first filter, we installed a small-volume, 0.5 micron filter at the inlet of the cavity (Valco filters for GC, ZBUFR1, VICI AG). Up to this date no degradation of the quality of CH_4 mixing ratio measurements could be detected."

11

Referee #2: Page 224, Lines 18 – 27 (Figure 4b). The +25 ppbv bias is disturbing and well discussed in the paper. However, it is critical that this bias remain constant for this technique to be adopted. Is there any longer-term data suggesting that this bias remains at +25 ppbv? If not, does the setup need to be calibrated using a GC system during every run?

Stowasser et al.: The data in Fig.4b shows 25 consecutive runs. This data was collected over a period of 24 hours without a change in the bias. This shows that the setup does not need to be calibrated using a GC system during every run, maybe not even once per day.

We added the information that this data set has been recorded over a period of 24 hours on p. 224, l.19.

Additionally, we have analyzed more data (not shown) and the bias remained constant until the end of the field measurements ca. 5 days later.

12

Referee #2: General – It should be noted that the WS-CRDS instrument only measures $^{12}CH_4$ and does NOT measure $^{13}CH_4$. Thus, changes in the isotope ratio of methane will lead to erroneous methane readings. Please discuss this effect and its potential magnitude for ice core studies.

Stowasser et al.: The reviewer is correct that measurements are made on $^{12}CH_4$. Since measurements and standards are both made on the dominant isotopologue the effect is negligible, i.e. in the sub ppb range. We added the following sentence on p. 6, l. 20:

"Note that all measurements are made on the $^{12}CH_4$ isotopologue, and therefore neglect variations of δ^{13}C and δD (=δ^{2}H). However, given the natural isotopic abundances, combined with the small range of natural isotopic variation, the induced error is far below our detection limit."

13

Referee #2: Figure 1 – Please clarify to better describe the debubbler and pressure-decoupling unit. I realize that these are discussed in some of the references; however, a more detailed picture (and discussion) in this paper would be very beneficial to describing the system.

Stowasser et al.: We updated Fig.1: Included a more detailed drawing of the debubbler and the open split.

Additionally, we included more information in Sect. 2.1 "Experimental Setup Description”:

“In the warm laboratory of the CFA three peristaltic pumps and a debubbler (internal volume of ca. 0.8 mL) distribute the sample stream between several systems for chemical analysis (for details see Kaufmann et al. 2008, Schuepbach et al. 2009). In brief, the debubbler is a standard pipette tip sealed against ambient with a custom-made plug at the top including two holes for an inlet and outlet tube, respectively. The sample stream from the melt head enters through the inlet tube and air bubbles rise, driven by buoyancy, to leave the debubbler with some residual water through the outlet tube. Hence, no bubbles reach the tip of the pipette tip, where water is pumped away for analyses of chemical components and stable isotopes of water. An open split with small internal volume is installed downstream of the outlet tube and prevents pressure fluctuations in the debubbler that would affect the chemical analyses. From here the air and residual water (3.2 mL/min, ca. 50% air by volume) is pumped through a heated transfer line (to avoid freezing of the sample) towards a second warm laboratory where CH_4 mixing ratio analysis takes place.”

Technical Corrections

1

Referee #2: Page 214, Line 5: Change “is to a high degree automated,” to “is, to a high degree, automated,”

Stowasser et al.: Done.

2

Referee #2: Page 217, Line 5: Change “for in the field day to day calibration… to “for day-to-day calibration of the system in the field…”

Stowasser et al.: Done.

Interactive comment on Atmos. Meas. Tech. Discuss., 5, 211, 2012.