**Atmospheric
Measurement
Techniques
Discussions**

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

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Answer to W. Euster's (Referee) comment on amtd-5-211-2012

We thank W. Euster for his careful reading of the manuscript, and the many thoughtful comments.

3.1

W. Euster: I found Figs. 5, 6 and 7 unclear and would like Peter Werle to have a look at these:

- *Panels (a) are "normalized" responses, but the units are ppbv. I would have expected a dimensionless number (fraction from 0 to 1), but since no mention could be found in the text on how the "normalization" was done, this could be a wording error as well.*

- *Panels (b) show d/dt of the "normalized" responses, in ppbv/s, and the numbers are to be multiplied by 10^{-3}, which makes that the range goes from –0.006 to 0.01 ppbv/s. I have a hard time to judge whether this is correct or whether the wrong impression I get has to do with the units (where does ppbv come from if values were normalized?). Moreover, in the text you use dm/dt, so the same notation should be used in the y-axis label.*

- *Panels (c) are explained to show the transfer function, but again I do not expect a transfer function to have units of ppbv. In fact, Eq. (5) shows $\hat{G}(f)$ as the transfer function, in which m' has units of 1/s (from Eq. (4)) which in Eq. (5) are multiplied with dt in seconds to yield a dimensionless function as expected. So my best guess is (as in the other panels) that the units in the Figures are wrong.*

- *Also in panels (c) I have a conceptual problem: if I use a transfer function for a signal, then I should not see a noise at the high frequencies (that's the concept of the red line in Fig. 5c). So why should $\hat{G}(f)$ be termed a "transfer function" if it transfers the signal as expected at low frequencies but not at high frequencies?*

Stowasser et al.:

- The labels are indeed a wording error. Due to the normalization, the y values in panels (a) are dimensionless numbers. We changed the y label to $m_{norm}(t)$ to indicate that this is the normalized measured signal.

- This also leads to units of 1/sec in panels (b). The y labels are changed to $d/dt(m_{norm}(t))$.

- Yes, also in panel (c) the y values are dimensionless. We changed the label to abs($\hat{G}(f)$).

- In panels (c) we show two transfer functions. The red line represents the transfer function of the modeled, noise-free signal (from the cdf fit to the normalized step). The black line represents the transfer function of the measured, noisy signal.

Due to the noise in the measurements, we cannot distinguish patterns in the measured signal that are hidden in the noise. This also shows up in the transfer function of the measured signal (black line), where frequencies of the noise are blown up (the high frequencies). True patterns in the measured signal with frequencies comparable to, or smaller than the noise frequencies can therefore not be detected without applying deconvolution techniques to the data.

P. Werle added the following to this comment: When looking at Fig 7c at the light grey transfer function, there seems to be a "noise floor" at 10^{-2}, which is white, i.e. frequency independent and therefore flat. In contrast in figure 5c/6c, the noise floor is "pink", i.e. frequency dependent and increasing. This should be discussed.

Stowasser et al.: The noise floor in the transfer function of the modified analyzer plus front-end in Fig.5c and 6c is frequency dependent and increases with noise. It looks like blue (violet) noise since it roughly scales with f in the transfer function.

In Fig.7c we see a white noise floor in the transfer function of the original analyzer. Unfortunately, we cannot see the noise floor of the transfer function of the modified analyzer, because we are limited by the sampling rate. Hence we cannot determine whether the origin of the violet noise floor lies in the modified analyzer or the front-end of the experimental setup.

<center>C578</center>

As we cannot determine the origin of the different noise floor, we decided to mention only the observation in the revised manuscript on p.24:

"For frequencies larger than ca. 0.01 s^{-1} the transfer function of the original analyzer shows flat (white) noise, which is independent of frequency (green squares in Fig.7c). However, the transfer function of the modified analyzer plus front-end shows frequency-dependent noise (Fig.5c and Fig.6b). For frequencies f larger than ca. 0.01 s^{-1} the transfer function scales approximately with f. We cannot determine whether the cause of this noise behavior lies in the modified analyzer or the front-end."

P. Werle: Also there is a change from frequency 1/s in fig 5/7 to wavenumber 1/cm in fig 6. It may be useful to harmonize this as the "time constant" (...kyr BP) may also be reflected in the Fourier time domain.

Stowasser et al.: To maintain consistency throughout the figures, we changed the bottom x-axis in Fig. 6 to time (A) and frequency (B). We added a second x-axis on top showing distance (A) and wavenumber (B).

We decided to use distance/wavenumber in Fig.6 for the following reason: Most researchers, who measure gases from ice cores, state their measurement resolution in cm. By using distance and wavenumber in Fig.6 we like to make it easier for those scientist to compare the measurement resolution to their own system. We state on p.230, l.22-23 how we convert from measurement time to measurement distance.

3.2

<center>C579</center>

W. Euster: In my understanding the dimensions and configuration of the hydrophobic membrane module are a key element for the performance of such a device. However, the authors only sloppily write "The performance of the gas extraction module depends on the pressure gradient over the hydrophobic membrane." (p. 215, l. 21–22). I'd appreciate if you could elaborate in more detail which considerations in your set-up let to a selection of a 0.5x1 (units?) MicroModule.

Stowasser et al.: We choose the MicroModule 0.5"x1" (the units are inches, included in revised manuscript) for gas extraction since it was the smallest gas extraction module we found on the market. The 0.5"x1" type is designed to degas a water stream of 30 mL/min and is therefore in best agreement with our system requirements. Moreover, we chose the smallest module to minimize internal sample dispersion. Laboratory tests showed, that the MicroModule extracts all bubbles from the sample stream of 3.2 mL/min (ca. 50% air by volume) at the given pressure gradient of 300 mbar across the membrane.

We added the following information on page 215, l.18: "With its internal volume of 5.4 mL, the MicroModule is small compared to other commercial systems for gas extraction and well-suited to degas small sample streams."

And on page 216 l.5: "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."

We also estimated the amount of dissolved methane molecules (see answer to Referee #2). In the paper on p.9 we refer to this estimation. 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.

3.3

W. Euster: You mention several times that the commercially available analyzer measures CH4|CO2|H2O, but you never explain why you still want to have a Nafion drier in the line which may simply smear out your signal. Or does the instrument not correctly correct for H2O effects without the Nafion drier? Please elaborate.

Stowasser et al.: Indeed, the instrument does not correct for H_2O effects. Especially under high water vapor concentrations, as we find after the wet gas extraction technique, the absorption feature of H_2O overlaps with the absorption feature of CH_4 that is used for mixing ratio analysis. A detailed description of this correction can be found in the "Water vapor correction white paper" by C. Rella (2012) (http://www.picarro.com/gas_analyzers/co2_ch4_h2o). We did not want to add a H_2O correction step with additional uncertainties to our data analysis, and instead decided to dry the sample.

We added the following sentence in Section 2.1. Experimental setup description (p.216, l.8) and added the corresponding reference: "By drying the sample, an otherwise necessary water vapor correction can be avoided (for more details about the water vapor correction see Rella, 2010)."

3.4

W. Euster: It remains unclear whether the authors were sponsored by Picarro or whether the collaboration was only related to the adjustment of the fitting software to the lower cavity pressure that the authors selected. Please specify in the acknowledgments if you received finances from Picarro (e.g. special rebate or free instrument) – or declare independence if this can be claimed.

Stowasser et al.: This study was not sponsored/financed by Picarro, other than Picarro adjusted the fitting software for us at no cost.

We added to the acknowledgements:

"We like to thank Eric Crosson, Chris Rella and Aaron van Pelt from Picarro Inc. for their support of this work. The authors did not receive any financial support from Picarro for the work presented in this study."

4. Minor issues

W. Euster: p. 213, l.20: What does $\pm13\text{-}36$ ppbv mean? Is it the $\pm1\sigma$ or the 95% confidence range that is expressed? Or something else?

Stowasser et al.: Güllük et al. used their optical method to measure CH_4 mixing ratios from two different ice cores from Vostok, Antarctica. As uncertainties (standard deviations) for these two measurements they state ±13 ppbv and ±36 ppbv, respectively. The latter, higher uncertainty is according to the authors due to an age difference of the ice samples.

<center>C582</center>

We wrote: "Uncertainty of CH_4 mixing ratio measurements with this method varies between ±13 ppbv and ±36 ppbv , depending on the age of the ice (Güllük, 1998)."

W. Euster: p. 222, l.4-5: What is meant with "the cavity pressure cannot be maintained constant"? Do you mean the pressure is too high or too low, or is it too variable around the correct set point?

Stowasser et al.: The latter is what we meant: The pressure cannot be stabilized, i.e. the pressure is varying around the set point. In the revised manuscript it now reads: "…the cavity pressure is unstable and fluctuates around the set point."

W. Euster: p.222, l.21: replace unfeasible with inacceptably

Stowasser et al.: We replaced "infeasible" with "unacceptably".

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