Interactive comment on "Comparison of nitrous oxide (N2O) analyzers for high-precision measurements of atmospheric mole fractions" by B. Lebegue et al.

Anonymous Referee #3

Received and published: 25 November 2015

This paper describes testing and comparisons of several methods for the measurement of nitrous oxide in the atmosphere. Resolving small gradients in the remote troposphere is a particularly challenging. As optical instruments have recently been developed, there is hope for improvement over traditional methods. Overall, this is a well-written and timely paper.

We would like to thank the reviewer for having reviewed this paper and formulated helpful comments. We answer each of them hereafter and add when needed the modifications in the revised version.

General comments: The sections focusing on testing (repeatability, drift assessment, long-term stability, effect of humidity) are interesting and useful. In section 3.4, it might be worth repeating that these tests were performed under controlled conditions (little variation in temperature?). We will add the following sentence:

P10952 L16-17 For each instrument, a target gas was measured regularly (at least twice a day) alternating with ambient air for several days in our temperature controlled laboratory.

For the short-term repeatability tests, were 15-20 minute periods chosen because this corresponds with the Allan variance minima for most instruments? Or, perhaps it was necessary to wait 15-20 minutes between wet (ambient) and dry (tank) samples. If either are true, it should be stated explicitly.

From our previous experience with the other analyzers tested at our laboratory, we determined that 15 to 20 minutes is sufficient for all analyzers to stabilize and to have at least 5 useable minutes. While some analyzers are stable within one minute, we define an identic period for all analyzers in this test. It is not due to wet ambient measurement as, as is said on page 10952 line 2, we alternate between target gas and dry ambient air. We will add a sentence to explain our choice of periods.

P10952 L2 From our experience with other analyzers, 15 to 20 minutes should be appropriate for all instruments to stabilize and to provide at least 5 minutes of stable measurements.

The air comparison could use more explanation. I think the authors should comment on how reliable these results are considering that some comparisons are based on measurements of dry air, while some are based on wet air with factory water vapor corrections, which, except for QC-TILDAS, you have shown are not adequate. You mentioned that the water vapor during the third period was < 1% (winter), but I suspect that water vapor was at least as high during the second period (May), yes?

We confirm that the water vapor was between 0.7 and 1.6 % during the second period. We will add this information in the paper.

P10959 L28 ... by the correction algorithms provided by the manufacturers (between 0.7 and 1.6 % of water vapor during the period).

Thus, I'm surprised that the dispersion of ICOS-EP/FTIR results shown in Fig. 6 are so tight, considering that the comparison involved ambient (wet) air. From figure 4, we could expect positive bias of up to ~ 0.5 ppb as water vapor approaches 2%. Thus, I would expect to see a tail on the negative side of the distributions in Fig. 6 for these instruments. For the ICOS-EP40 we can see in the water vapor correction assessment (Figure 4) that between 0.7% and 1.6% of water vapor, the difference to the true value stays around 0.4-0.5 ppb. So there, if we apply our water vapor correction, we will go from a difference of -0.21 ppb between the FTIR and ICOS-EP40 to a difference of ~0.2 ppb. But the water vapor correction is almost constant between 0.7 and 1.6% of water vapor, so it will not affect the distribution.

For the ICOS-EP38, we can see with the time series (shown in the new figure 6 latter in our answers to your comments) two periods during the air comparison. During the first one (3 May to 7 May) the water vapor was between 0.7 and 1.2 % while during the second one (7 May to 9 May) the water vapor was between 1.1 and 1.6 %.

Further, the slopes shown in Table 8 suggest real calibration differences. But these could also be related to water vapor, so how relevant are the slopes shown in Table 8? If you choose to report them, I suggest including an uncertainty and the N2O range measured. Alternatively, it might be better to replace Table 8 with a figure showing mole fraction differences as a function of time, or instrument X vs FTIR as a scatter plot with r-squared shown in each plot.

Table 8 will be removed and all mention of it in the last paragraph in section 3.9 will be removed. Instead a time series plot with the difference between the FTIR and each other instrument will be added to the histogram plots (Figure 6).

Specific comments: p. 10945, line 18: check text: "mid infrared vs mid-infrared"; "sweeps in the frequency"

We will correct line 18 and remove "in the frequency through"

p. 10948, line 28: I'm confused by the term "scale" here. Clearly you have different sets of calibration standards. Are they all referenced to the same scale, i.e. WMO X2006A, but by various pathways? Or is the MPI scale independent (p. 10949, line 4?).

We will change "scale" (line 28) to "set of calibration". All calibration gases and measurements are reported on the NOAA-2006A scale. We will also modify the term MPI scale for calibration gases determined by MPI, which was used not correctly.

p. 10953, line 14: should "decreased to" be replaced with "decreased by"?
We will clarify the sentence.
P10953 L13 For a calibration every 12 hours, the LTR improved to 0.07 ppb,...

p. 10955, line 1: replace "constructors" with "manufacturers" We will rephrase as suggested.

p.10975, fig. 1: Are the vertical lines on the lower figure necessary? They don't seem to correspond with anything.

They represent an averaging time of 1 min and 1 hour. We will add a sentence in the legend of figure 1.

P10975 End of the legend: "The two vertical lines in the lower panel correspond to an averaging time of 1 min and 1 hour."

Table 6: It might be useful to include the short term repeatability (1-min) in this table so that it would be clear from the table why some instruments could not reach the 0.1 ppb target. For the stabilization time, the STR have no influence. Here we do continuous measurements to see when the instrument reaches the final value, and the value called 2σ in the table correspond to two times the CMR value (for 1 minute measurements). The legend in table 6 will be modified to be clearer:

"at either ± 0.1 or 2σ (from CMR test (1min value)) ppb of the final value."

Table 8: Not sure that the intercept is all the important in this table. However, I would suggest that an uncertainty on the slope could be included. I would also suggest showing expanded time series or differences between instruments during the air comparison, so the reader could then see the range of N2O measured.

Table 8 will be removed and we will add the time series and differences to figure 6.





We will add: All data have been automatically corrected for water vapor using the manufacturer correction.