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

Anonymous Referee #2

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The manuscript 'Comparison of nitrous oxide (N2O) analyzers for high-precision measurements of atmospheric mole fractions' by B. Lebegue et al. presents a comprehensive comparison between literally all currently available measurement techniques for nitrous oxide. It is a very valuable contribution to the atmospheric measurement community, and well suited for publication in AMT after considering the following mainly minor comments.

We would like to thank the reviewer for his helpful comments on this manuscript. We answer each of them hereafter and add when needed the modifications in the revised manuscript.

General remarks: As already mentioned by the other reviewer, two manufactures are co-authors on this paper, whereas the other three manufactures are not. This probably originates from the fact that two instruments were directly provided by these manufactures. The manufactures of the other instruments should also have the chance to at least look at the results, and provide input if necessary. If this has not happened already, I recommend that the other manufactures are contacted before the final AMT paper goes online.

The two co-authors who are also instrument vendors have decided to withdraw from the co-author list as their contribution, apart from lending us their instrument, was minimal. The acknowledgment will be rewritten in order to acknowledge all the contributions from the various instrument providers:

This work has been funded by the InGOS EU project (284274). We acknowledge the financial support given by CEA, CNRS and UVSQ for ICOS France. Special thanks to David Griffith for his help during the installation of the FTIR (2011-2012) and for the help during later updates. We would like to thank Picarro Inc, especially Eric Crosson and Chris Rella for providing us the prototype of the N_2O G5101-i analyzer. We also want to thank Hj Jost and Thermo Fischer Scientific for providing us their N_2O IRIS 4600 analyzer. We are grateful to Macel Vanderschoot and three anonymous referees for their detailed and constructive reviews.

Specific comments: Page 10948, line 20: concerning the use of calibration gases with synthetic air matrix, the N2, O2, and Ar content should be specified. Spectroscopic techniques can be very dependent on the matrix, and it would be important to mention this somewhere in the paper.

The content of the synthetic air matrix will be added

P10949 L3 and L7: …filled with a synthetic matrix of 21.00 Vol.-% ± 1 % of O_2, 0.93 Vol.-% ± 1 % of Ar and a balance of N_2 (Deuste Steininger)…

Page 10953, Linearity assessment: Interestingly, the slope was changing quite significantly for some of the tested analysers. Do you have an explanation for this? This also stresses the need of two or more calibration gases, as you suggested.

In most of the cases the slopes do not vary significantly but it is true that some outliers are observed. It is important to note that the plots can be misleading since the range of the vertical axis varies from instrument to instrument. For example the range used for CRDS is

one order of magnitude lower than the one used for DFG. In several cases the variability of the slope appears to be related to the change of the calibration set, either the number of cylinders or the mole fraction range (e.g. QC-TILDAS, ICOS-EP38). As you mention, it emphasizes the importance of having several calibration cylinders spanning the proper range.

Figure 3, temperature dependence, and discussion in the text: There is some interesting structure in the QC-TILDAS instrument data, which has nothing to do with temperature dependence. Do you know the reason for this behavior?

Yes, the high frequency variations of N_2O are due to cell pressure variations.

A line will be added in the article:

P10956 L12 It should be noted that for the QC-TILDAS test, the high frequency variations of N_2O at the beginning and near the end are due to pressure variations inside the cell.

The conclusions that there is no temperature dependence for this instrument is probably not supported by the data you present here. It could well be that you see a dependence if you consider only the data where you have an actual temperature change. For future temperature dependence tests I would recommend that a temperature cycle is repeated at least three times.

The temperature sensitivity can be separated in two components: the true temperature dependence of the instrument and the disequilibrium caused to the instrument by a change in temperature. The steps in temperature are here to detect the true temperature dependence of the instrument.

We will change the temperature dependence recommendations:

P10957 L1 In this case, the room temperature needs to be monitored precisely, and the temperature dependence needs to be determined accurately by repeating two to three times the temperature test.

Figure 4, discussion of water vapour correction: It should be stressed here that the determination of the correction is always necessary when humid measurements are made.

Yes, if one decides to do wet ambient air measurements, the determination of the water correction will be necessary. The last sentence of the water vapor correction will be modified:

P10959 L5 However, if some stations or laboratories are sufficiently equipped to make their own instrument specific water vapor dependency test on a regular basis, wet air measurements could then be performed.

P 10959, line 2 states that a careful evaluation is not necessary for the QC-TILDAS and FTIR instruments. For the FTIR, I agree, since it has a built in dryer, but the QC-TILDAS must be checked, since there is the potential for instrument to instrument differences, and the correction can also be changed in the data acquisition software.

We will rephrase:

P10959 L2 …with the exception of the FTIR which has a built-in drying system. While the QC-TILDAS tested here showed a good water correction, users of this instrument should still test the water correction.

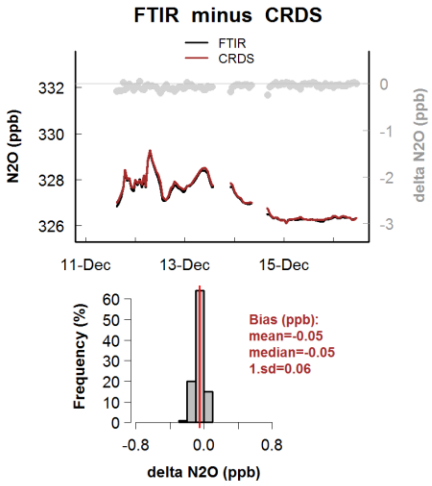
Air comparisons: If I understood correctly, no calibration of the instruments were made over the 100 h air comparison periods. The result therefore might depend on the time since the last calibration of the instrument. It would be good to have comparable conditions for all comparisons, e.g. an initial calibration at the beginning of the experiment.
We confirm that no calibration was made over the 100h air comparison periods. For all instruments a calibration was made a few days before and another a few days after. With the new time series plot for air comparison and the plots of linearity, it is possible to see when the different calibrations were made regarding the air measurement comparisons. The data was then calibrated by doing an interpolation between the previous calibration and the one after the comparison period.
We will add the following sentence:
P10960 L9 The data was calibrated by doing an interpolation between the calibration before and after the comparison period.

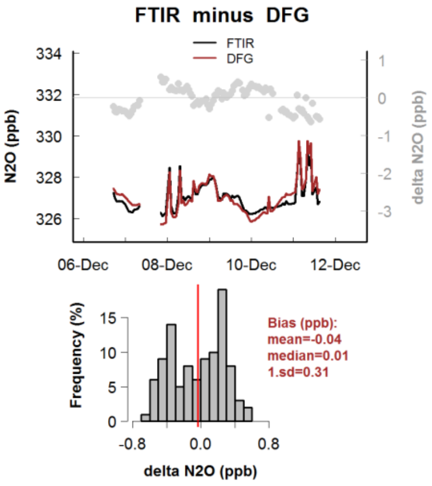
Furthermore, the manuscript is relatively vague concerning recommendations of the frequency of calibrations. It clearly seems that the results for many instruments would significantly improve if more frequent calibrations are performed.

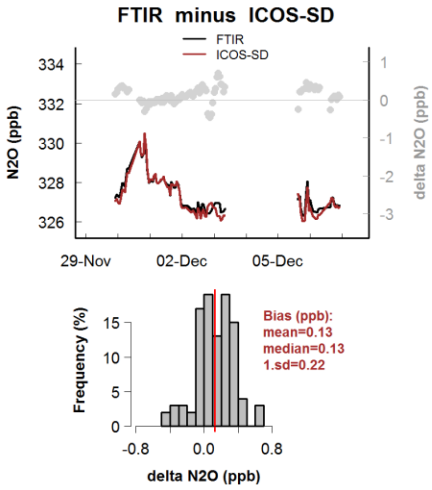
We agree, that especially the performance from the ICOS-EP would improve from more frequent calibrations. This is described in 3.5 and in the conclusion. In paragraph 3.5 and in the summary, we give information concerning the calibration frequency.
"The calibration strategy chosen for the test with a 14-day frequency is only acceptable for the CRDS, FTIR and QC-TILDAS. For the other instruments, a more frequent calibration strategy needs to be developed. The results showed that for an ICOS-EP, a calibration frequency of twice a day is necessary to reduce the LTR below the WMO recommendations."
In addition we have more information concerning the ICOS-EP in the conclusion:
"In our case, an injection frequency of 11 hours for a reference gas led to an improvement of the short-term repeatability of the target gas from 0.85 ppb to 0.07 ppb. Thus, prior to the use of an analyzer, the calibration strategy should be studied and optimized for the instrument and station conditions.

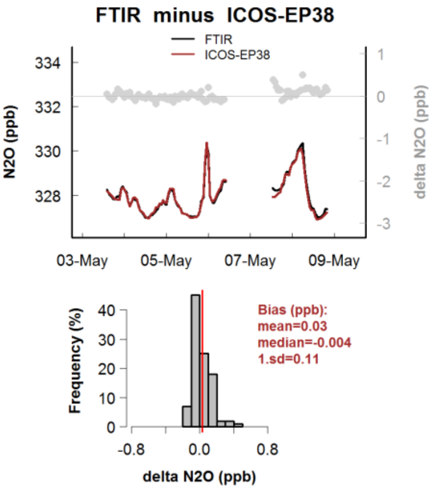
Furthermore, it also would be valuable to have a time series plot (including the difference) in addition to the deviation histograms. This would give additional information, and drift issues etc. can currently not be seen in the data presented for the air comparison.

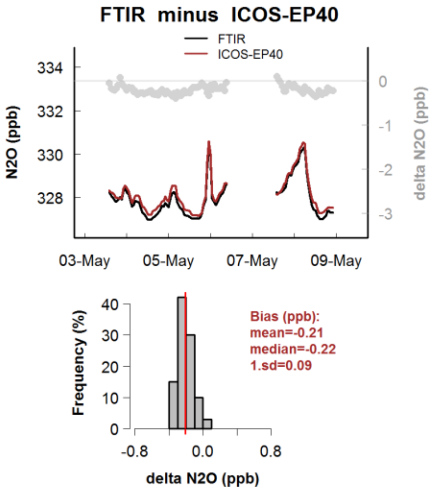
We will modify Figure 6, and will add a time series plot for each deviation histograms. Table 8 will be removed, as well as mentions to it in the last paragraph of the air comparison part.


FTIR minus CRDS
FTIR
CRDS
N2O (ppb)
332
330
328
326
delta N2O (ppb)
0
-1
-2
-3
11-Dec
13-Dec
15-Dec
Frequency (%)
60
50
40
30
20
10
0
-0.8
0.0
0.8
delta N2O (ppb)
Bias (ppb):
mean=-0.05
median=-0.05
1.sd=0.06


FTIR minus DFG
FTIR
DFG
N2O (ppb)
334
332
330
328
326
delta N2O (ppb)
1
0
-1
-2
-3
06-Dec
08-Dec
10-Dec
12-Dec
Frequency (%)
15
10
5
0
-0.8
0.0
0.8
delta N2O (ppb)
Bias (ppb):
mean=-0.04
median=0.01
1.sd=0.31


FTIR minus ICOS-SD
FTIR
ICOS-SD
N2O (ppb)
334
332
330
328
326
delta N2O (ppb)
1
0
-1
-2
-3
29-Nov
02-Dec
05-Dec
Frequency (%)
15
10
5
0
-0.8
0.0
0.8
delta N2O (ppb)
Bias (ppb):
mean=0.13
median=0.13
1.sd=0.22


FTIR minus ICOS-EP38
FTIR
ICOS-EP38
N2O (ppb)
334
332
330
328
delta N2O (ppb)
1
0
-1
-2
-3
03-May
05-May
07-May
09-May
Frequency (%)
40
30
20
10
0
-0.8
0.0
0.8
delta N2O (ppb)
Bias (ppb):
mean=0.03
median=-0.004
1.sd=0.11


FTIR minus ICOS-EP40
FTIR
ICOS-EP40
N2O (ppb)
334
332
330
328
delta N2O (ppb)
0
-1
-2
-3
03-May
05-May
07-May
09-May
Frequency (%)
40
30
20
10
0
-0.8
0.0
0.8
delta N2O (ppb)
Bias (ppb):
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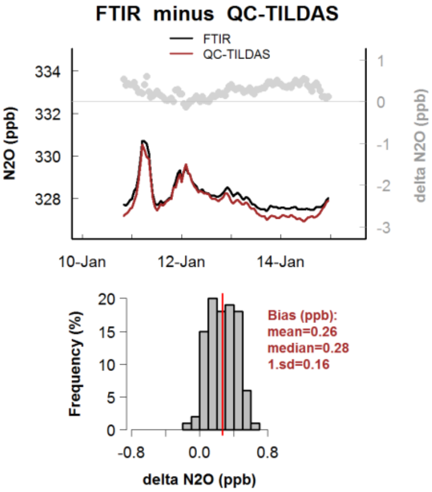
median=-0.22
1.sd=0.09


FTIR minus QC-TILDAS
FTIR
QC-TILDAS
N2O (ppb)
334
332
330
328
delta N2O (ppb)
1
0
-1
-2
-3
10-Jan
12-Jan
14-Jan
Frequency (%)
20
15
10
5
0
-0.8
0.0
0.8
delta N2O (ppb)
Bias (ppb):
mean=0.26
median=0.28
1.sd=0.16